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POHCs (Principal Organic Hazardous Constituents) and PICs (Products of Incomplete Combustion) Screening Protocol

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16. ABSTRACT

The report describes risk-driven analysis strategies and a tiered survey approach of analyses that should be useful for building data bases related to other waste combustion processes. (NOTE: The need to characterize hazardous waste incinerator emissions for multiple organic compounds has been steadily increasing for several years. Similar interest is being shown in organic emissions from municipal waste incinerators and sewage sludge incinerators.) Seven protocols based on methods published by the EPA were developed and reviewed. The protocols included GC-FID and GC-MS screening for volatile compounds, Soxhlet extraction sample preparation, TCO determination, GC-MS screening for semivolatile compounds, gravimetric determination, and HPLC-UV screening. Application of the proposed scheme to environmental samples in this study was limited. Three extracts of samples obtained from Method 0010 testing of an incinerator under different feed and firing conditions were analyzed by five of the proposed protocols. Thirty-four compounds have been tentatively identified but, more importantly, the protocol methods seem to perform well.

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Organic Compounds	Stationary Sources	14G 14B
Selection	Hazardous Waste	
Data Acquisition	Risk-driven Protocol	15E
Incinerators	Products of Incomplete Combustion (PICs)	21B
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Toxicity		
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POHCs AND PICs SCREENING PROTOCOL

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FOREWORD

This report has been prepared by Southern Research Institute as part of U.S. EPA-68-02-3996, Work Assignment 2/017, in support of regulatory programs of the EPA's Air and Energy Engineering Research Laboratory at Research Triangle Park, North Carolina. The purpose of this document was to develop a generalized screening protocol for the analysis of organic compounds in combustion effluents. The sampling and analysis methods in this document are based on protocols developed and documented in EPA guideline documents and SW 846, Test Methods for Evaluating Solid Waste. The basic premise of this document was to use existing sampling and analysis techniques whenever possible and practical. This protocol is structured to give maximum information while minimizing time and cost incurred in the collection of adequate data. Furthermore, by using a tiered approach, the proposed protocol presents a foundation for a protocol that can be risk-driven.

ABSTRACT

The purpose of Work Assignment 2/017 under Contract 68-02-3996 is to develop a generalized screening protocol for the analysis of organic compounds in combustion effluents.

During the last decade, the destruction of hazardous waste has become an increasingly desirable alternative to classical hazardous waste disposal methods. Properly designed and operated incinerators destroy almost all hazardous waste organic compounds while reducing total waste volume. However, the improper design or operation of a hazardous waste incinerator may pose a risk to public health through hazardous emissions. Currently, trial burn protocols for an incinerator are designed to determine preselected Principal Organic Hazardous Constituents (POHCs) and not total organic emission. The purpose of this report is to present a proposed analytical protocol for use in screening total emissions from hazardous waste incinerators and combustion sources.

The sampling and analysis methods incorporated in this document are based on protocols developed and documented in EPA guideline documents and SW 846, Test Methods for Evaluating Solid Waste. The basic premise of this document is to use or modify existing sampling and analysis techniques whenever possible or practical. This protocol is structured to give maximum information while minimizing time and cost incurred in the collection of adequate data. Sections on the analysis of volatiles, semivolatiles, and nonvolatiles have been incorporated into the protocol. The analytical methods are based on GC/FID, GC/MS, and HPLC/UV whenever possible.

By using a tiered approach, this protocol presents a foundation from which a risk-driven protocol can be developed.

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ABBREVIATIONS AND SYMBOLS

amu	Atomic Mass Unit
BFB	4-Bromofluorobenzene
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
cm	Centimeter (10^{-2} m)
°C	Degrees Centigrade
DFTPP	Decafluorotriphenylphosphine
DRE	Destruction and Removal Efficiency
EPA	U.S. Environmental Protection Agency
g	Gram
GC/FID	Gas Chromatography/Flame-Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
hrs; (h)	Hour
HPLC/Fluorescence	High-Performance Liquid Chromatograhy/ Fluorescence Spectrometry Detection
HPLC/MS	High-Performance Liquid Chromatography/ Mass Spectrometry
HPLC/UV	High-Performance Liquid Chromatography/ Ultraviolet Spectrometry Detection
ID	Internal Diameter
IS	Internal Standard
m	Meter
MDL	Method Detection Limit
µg	Microgram (10^{-6} g)
µL	Microliter (10^{-6} L)
µm	Micrometer (10^{-6} m)
mg	Milligram (10^{-3} g)
mL	Milliliter (10^{-3} L)
mm	Millimeter (10^{-3} m)
min	Minute
MM5	Modified Method 5 Sampling Train
ng	Nanogram (10^{-9} g)
POHCs	Principal Organic Hazardous Constituent(s)
PICs	Product(s) of Incomplete Combustion
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RF	Response Factor
RRT	Relative Retention Time
RSD	Relative Standard Deviation
SASS	Source Assessment Sampling System
sec; (s)	Second
SRI	Southern Research Institute
SS	Surrogate Standard
TCO	Total Chromatographable Organics
TIC	Total Ion Chromatograms
VOST	Volatile Organic Sampling Train

I. INTRODUCTION

During the last decade, the destruction of hazardous waste by incineration has become an increasingly desirable alternative to classical hazardous waste disposal methods such as landfilling, lagooning, and deep well injection. Properly designed and operated incinerators destroy almost all of the hazardous organic compounds of waste streams while reducing total waste volume. Potential recovery of energy and materials such as hydrochloric and sulfuric acid are also pluses. However, the improper design or operation of a hazardous waste incinerator may pose a risk to public health through the emission of potentially hazardous chemicals into the atmosphere. In the United States, the destruction of hazardous waste by incineration is regulated by the Resource Conservation and Recovery Act (RCRA) of 1976. RCRA requires that the destruction and removal efficiency (DRE) of an incinerator, for certain predetermined Principal Organic Hazardous Constituents (POHCs), be equal to or greater than 99.99%.

Normally, during a trial burn of an incinerator for certification, one to six POHCs per waste stream are chosen for study. The success of a trial burn depends on meeting the DRE criteria and other environmental regulations for these designated POHCs. In general, most designated POHCs are volatile or semivolatile organic compounds amenable to gas-chromatographic analysis methods. However, some POHCs may require analysis by high-performance liquid chromatography or by compound-specific methods. Designated POHCs chosen to be measured in a trial burn of a waste are usually those POHCs which are the most difficult to burn or those which have the highest concentrations. Occasionally a POHC is unique to a particular waste and is selected on that basis. Currently, trial burn results for specific designated POHCs are being interpreted to be applicable to other organics in the waste stream that are less difficult to burn. Thus, total incinerator emissions are not routinely determined in trial burns.

Currently, trial burn protocols are designed to determine preselected POHCs in a hazardous waste incineration trial burn. The development of a screening protocol would allow for the analysis of preselected POHCs and for the analysis of all other major constituents of the combustion effluent. Generally, the total composition of a combustion effluent is unknown at the time of a trial burn. Compounds in the combustion effluent may be compounds derived from auxiliary fuel, compounds originally present in the hazardous waste, and compounds formed in the combustion process. Compounds not originally present in the hazardous waste or fuel but detected in the stack emissions are designated as products of incomplete combustion (PICs). A screening protocol must measure all of these elements in a way to identify the major emissions (POHCs and PICs) and certain specific highly toxic compounds that may be present at a lower concentration.

Protocols are available for conducting a trial burn plan and for the sampling and analysis of specific designated POHCs. All the elements of the sampling and analysis protocols for a trial burn plan can be extended and incorporated into a screening protocol. The basic "building blocks" from which

a cost-effective screening protocol can be assembled have been developed for hazardous waste incineration programs.

Screening analysis is designed to identify and quantify species that are present in process emissions and are of potential concern in assessing the risk to health and the environment. The purpose of this research is to develop an analytical protocol for use in screening emissions from hazardous waste incinerators and combustion sources.

In this report, we present the results of a tiered approach to the screening of combustion effluents which must be the initial phase in the development of a risk-driven protocol.

CONCLUSIONS:

The purpose of this program was to develop a generalized screening protocol for organic compounds in combustion effluents. We developed a tiered approach to the screening protocol based on simple prescreening techniques. Driven by the quantity of pollutants found in the prescreening of the samples, we proceeded to more involved and specific analytical techniques. We evaluated GC/FID, GC/MS, HPLC/UV, and HPLC/MS as candidate screening methods.

We applied the proposed protocol to the analysis of incinerator effluent sample extracts. We determined the relative quantity of organic pollutants in each sample. The major pollutants were identified and quantified.

Our evaluation of combustion effluent samples by the proposed tiered approach both supports the need for a screening protocol and represents the initial phase in the development of a risk driven-protocol for the screening of all combustion effluents.

RECOMMENDATIONS:

- The proposed protocol should be peer reviewed to determine strength and deficiencies in meeting risk assessment requirements.
- The proposed protocol should be refined, as deficiencies are identified, and the revisions should be confirmed in the laboratory.
- The revised protocol should be evaluated with incinerator effluent samples including
  - samples from incineration of different waste types
  - samples from similar waste, destroyed in incinerators of different design
- Finally, the proposed method should be evaluated with incinerator effluent samples fortified at a concentration corresponding to each "decision level" to evaluate method performance.

II. APPROACH TO SCREENING PROTOCOL

In recent years, EPA has moved toward a risk assessment and a risk reduction framework for making regulatory decisions concerning the disposal of hazardous wastes. Previous studies have demonstrated that hazardous waste incinerator facilities perform well relative to the DRE requirement. However, this approach does not address the potential for the formation of toxic compounds in combustion effluents. These compounds may be formed by partial oxidation or recombination reactions during the incineration process.

EPA's Science Advisory Board has also commented on the lack of information on total emissions from incineration processes. A general sampling and analysis screening protocol is needed to satisfy requirements for data on total emissions from incineration processes. A screening protocol must be able to identify and quantify the major organic compounds in combustion effluents.

There are no official procedures for screening analyses of combustion effluents. There is, however, a substantial volume of data based on many of EPA's established procedures such as EPA Methods 624 and 8240 for volatiles and EPA Methods 625 and 8270 for semivolatiles. EPA Contract Laboratory Program (CLP) Protocols are based on similar analytical methods. Routinely CLP sample extracts are analyzed for 65 semivolatile and 37 volatile compounds. In addition, the results of these analyses can be used to tentatively identify unknown compounds in the sample and make semi-quantitative estimates of concentrations. Although the number of unknown compounds to be identified can be arbitrary, usually all compounds with peak heights >10% of the nearest internal standard response are considered. Alternately, a designated number of compounds (10 to 20) can be specified for identification.

The purpose of this document is to develop a generalized screening protocol for organic compounds in combustion effluents. The sampling and analysis methods in this document are based on protocols developed and documented in EPA guideline documents and SW 846, Test Methods for Evaluating Solid Waste. The basic premise of this document is to use existing sampling and analysis techniques whenever possible and practical. This protocol is structured to give maximum information while minimizing time and cost incurred in the collection of adequate data. Furthermore, by using a tiered approach, the proposed protocol presents a foundation for a protocol that can be risk-driven.

Figure II-1 is a flow diagram of the overall Organic Screening Protocol. Extraction and analysis procedures for volatiles, semivolatiles, and nonvolatiles have been incorporated into the overall screening protocol. This protocol assumes that specific sampling methods and procedures (such as VOST, MM5, or SASS trains) have been defined and implemented.

Figure II-2 is a detailed overview of the volatiles section of the overall protocol. Tier 1A outlines the GC/FID screening procedure. Tiers 2A, 3A, and

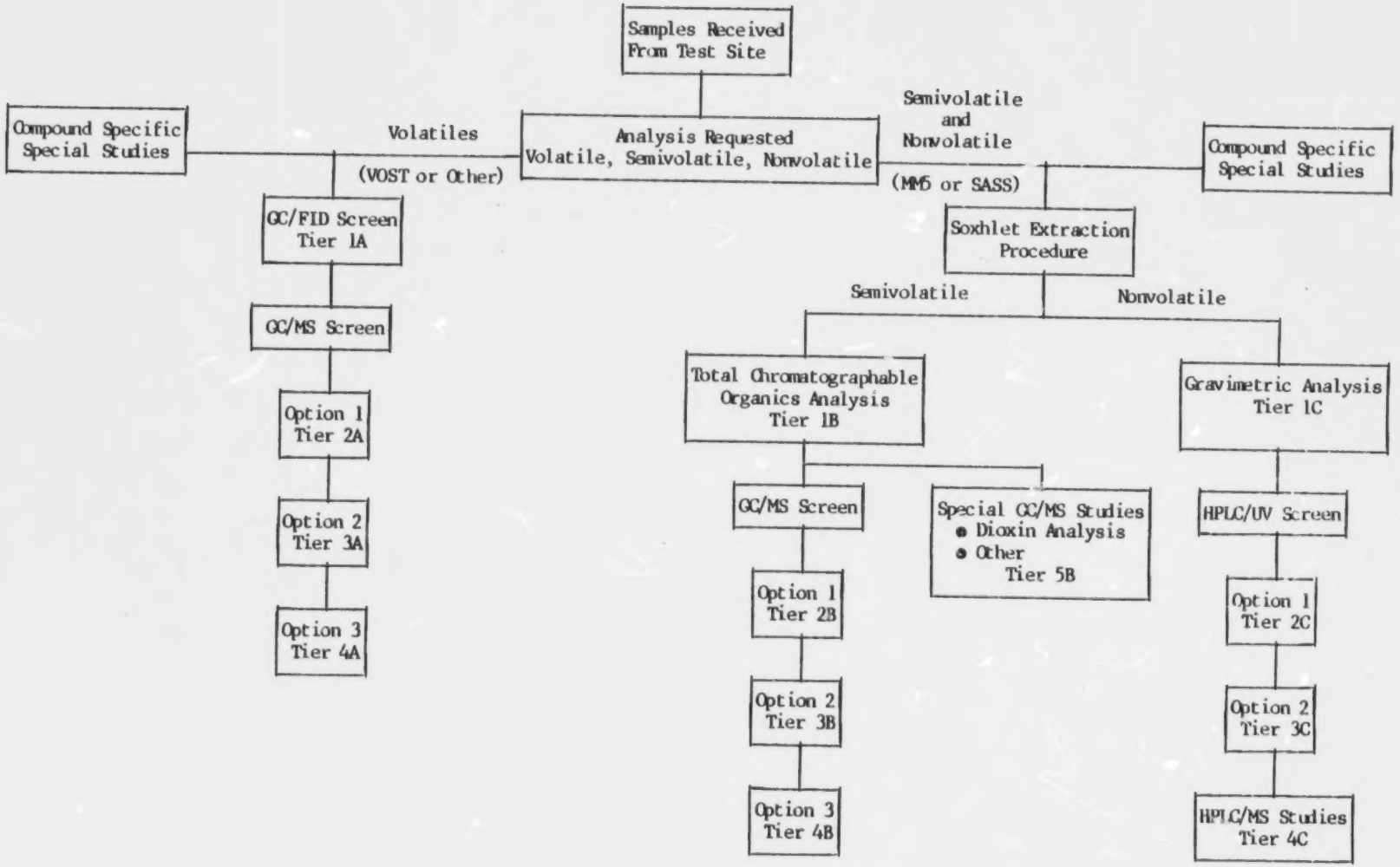

Figure II-1. Flow diagram for the Organic Screening Protocol.

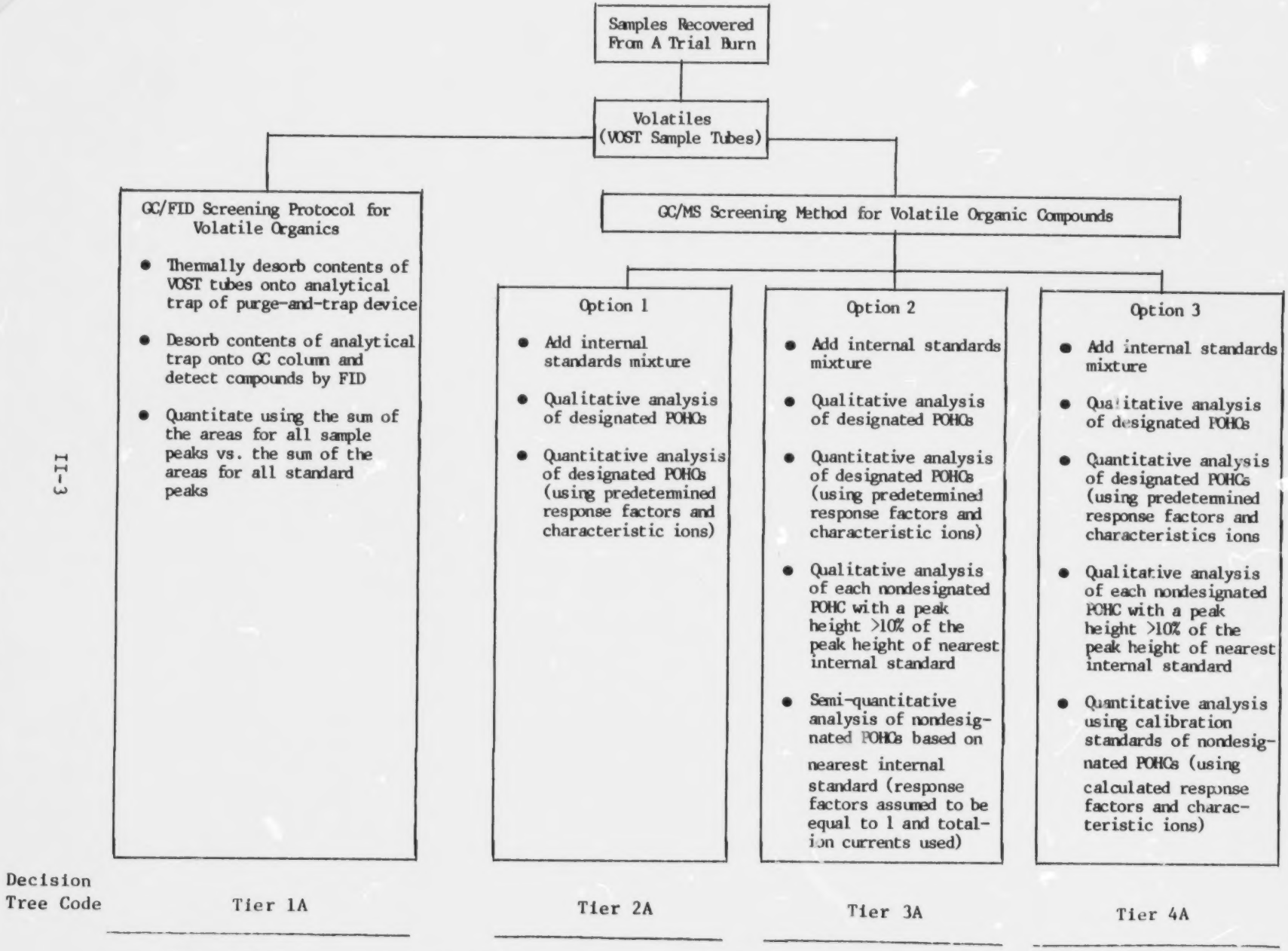
Samples Recovered From A Trial Burn
Volatiles (VOST Sample Tubes)
GC/FID Screening Protocol for Volatile Organics
• Thermally desorb contents of VOST tubes onto analytical trap of purge-and-trap device
• Desorb contents of analytical trap onto GC column and detect compounds by FID
• Quantitate using the sum of the areas for all sample peaks vs. the sum of the areas for all standard peaks
GC/MS Screening Method for Volatile Organic Compounds
Option 1
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristic ions)
Option 2
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristic ions)
• Qualitative analysis of each nondesignated POHC with a peak height >10% of the peak height of nearest internal standard
• Semi-quantitative analysis of nondesignated POHCs based on nearest internal standard (response factors assumed to be equal to 1 and total-ion currents used)
Option 3
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristics ions
• Qualitative analysis of each nondesignated POHC with a peak height >10% of the peak height of nearest internal standard
• Quantitative analysis using calibration standards of nondesignated POHCs (using calculated response factors and characteristic ions)
Decision Tree Code
Tier 1A
Tier 2A
Tier 3A
Tier 4A

Figure II-2. Proposed volatile screening protocol for POHCs and PICs from combustion sources.

4A are different options within the GC/MS volatiles screening method. Option 1 (Tier 2A) allows for the qualitative and quantitative determination of designated POHCs. Option 2 (Tier 3A) allows for the qualitative and quantitative determination of designated POHCs and the qualitative and semi-quantitative determination of non-designated POHCs. Option 3 (Tier 4A) allows for the qualitative and quantitative determination of designated and non-designated POHCs. Figure II-3 is a decision tree flow diagram for the volatile analyses. Risk assessment data can be incorporated into the flow diagram at the decision points to help one determine if sufficient data have been obtained.

Figure II-4 is a detailed overview of the semivolatiles section of the overall protocol. Tier 1B is a total chromatographable organics screening method based upon solvent extraction and analysis by capillary column GC/FID. Tiers 2B, 3B, and 4B are different options within the GC/MS semivolatiles screening method. Option 1 (Tier 2B) allows for the qualitative and quantitative analysis of designated POHCs. Option 2 (Tier 3B) allows for the qualitative and quantitative analysis of designated POHCs and the qualitative and semi-quantitative analysis of non-designated POHCs. Option 3 (Tier 4B) allows for the qualitative and quantitative analysis of both designated and non-designated POHCs. Tier 5B incorporates special non-routine GC/MS methods of analyses for compounds or groups of compounds such as dioxins and furans. Figure II-5 is a decision tree flow diagram for the semivolatiles section of the overall screening protocol. Risk assessment data can be incorporated into the protocol to help one determine if sufficient data have been obtained.

Figure II-6 is a detailed overview of the nonvolatile section of the overall screening protocol. Tier 1C is a Gravimetric Analysis Method for total nonvolatile organic content. Options 1 (Tier 2C) and 2 (Tier 3C) are HPLC/UV screening methods for nonvolatile organics. In Option 1 designated POHCs are qualitatively identified by retention time comparisons with standards and are quantitated using external standard calibration curves. Option 2 is the same as Option 1 with the addition of a semi-quantitative analysis of non-designated POHCs based on the calibration curve of the nearest designated POHC. Tier 4C includes special studies by HPLC/MS for the identification of nonvolatile non-designated POHCs. This section of the protocol will require further refinements as advances are made in analytical techniques using HPLC/MS. Figure II-7 is a decision tree flow diagram for the nonvolatile section of the overall screening protocol. Risk assessment data can be incorporated into the protocol to help one determine if sufficient data have been obtained.

Section 3 of this report contains detailed analytical procedures for different analyses in the screening protocol. Each analytical procedure has been written as a stand-alone document and is based on existing sampling and analysis techniques wherever possible. Procedures from SW 846, Test Methods for Evaluating Solid Waste, were used whenever possible. These analytical procedures may be used for most of the compounds in Appendix 8, Part 261, 40 CFR. Predicted analytical methods for each POCH are summarized in the Appendix.

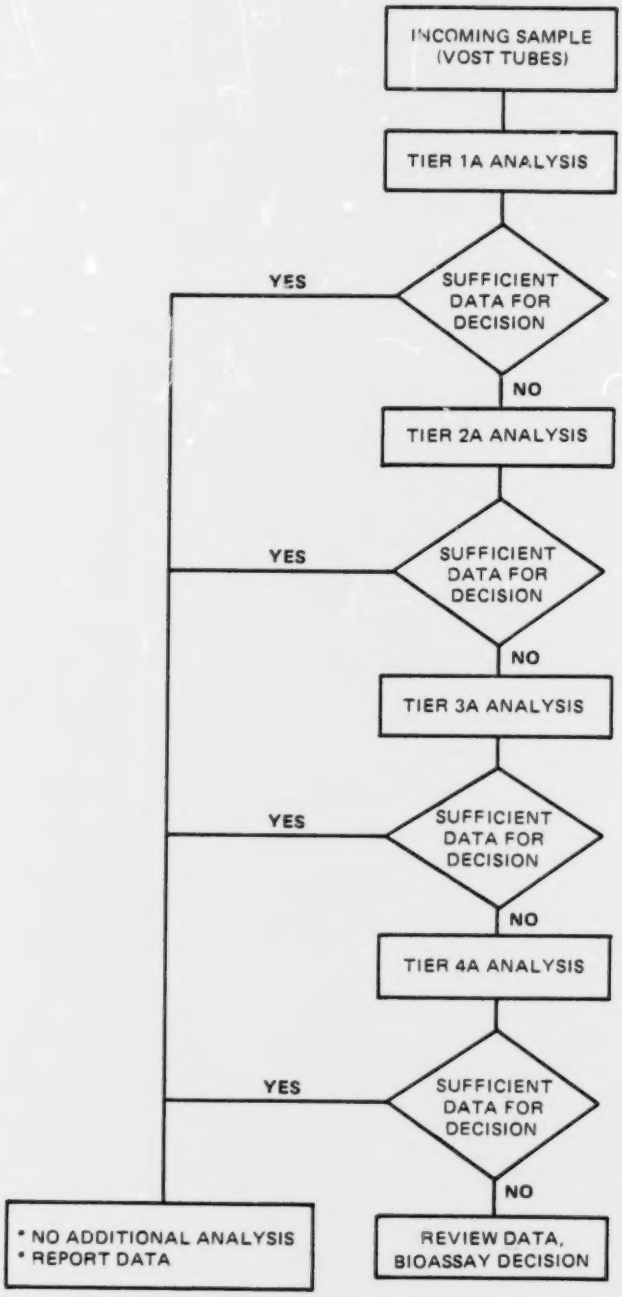

Figure II-3. Decision tree for volatiles.

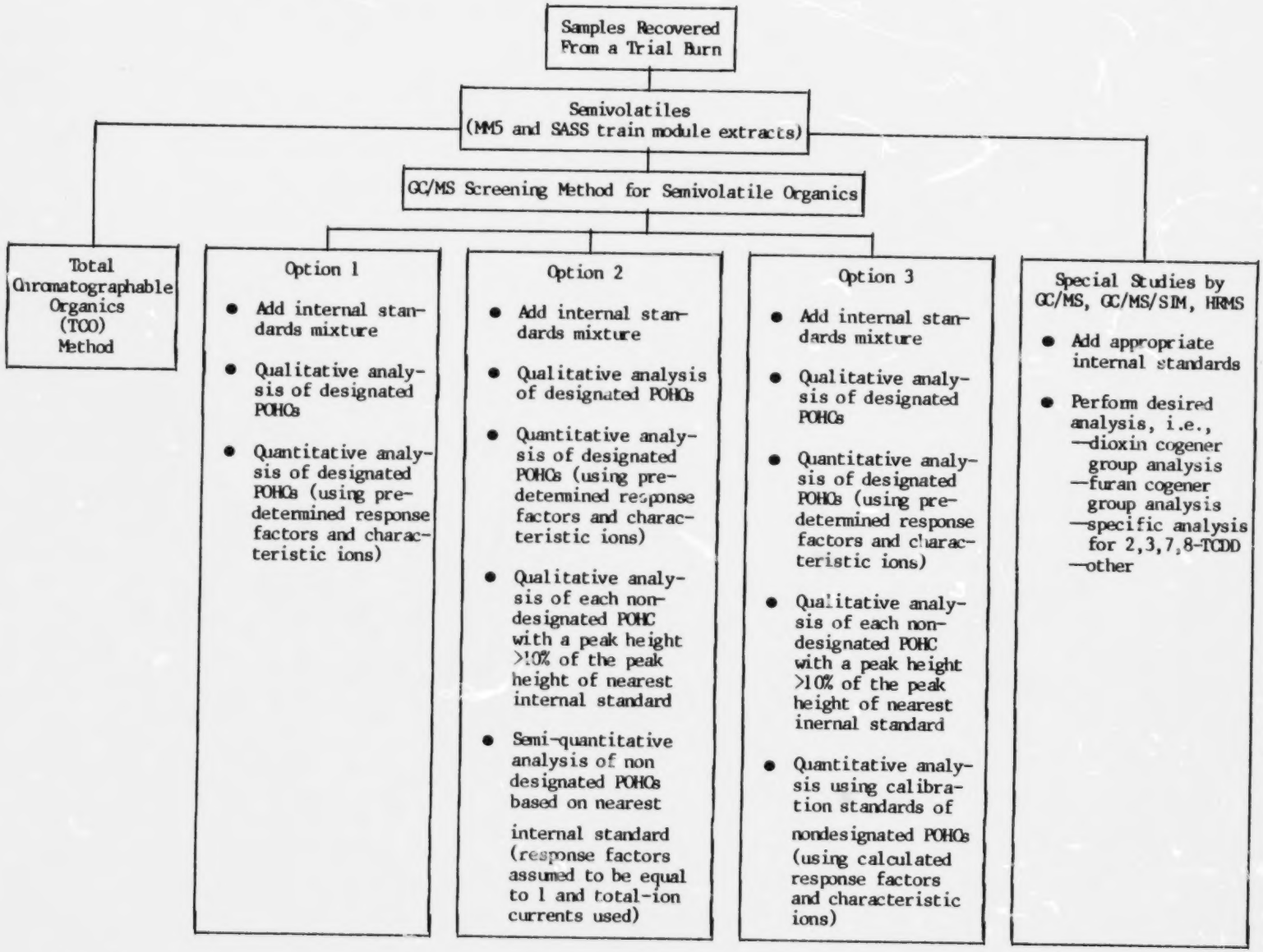
Samples Recovered From a Trial Burn
Semivolatiles (MM5 and SASS train module extracts)
GC/MS Screening Method for Semivolatile Organics
Total Chromatographable Organics (TCO) Method
Option 1
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristic ions)
Option 2
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristic ions)
• Qualitative analysis of each nondesignated POHC with a peak height >10% of the peak height of nearest internal standard
• Semi-quantitative analysis of non designated POHCs based on nearest internal standard (response factors assumed to be equal to 1 and total-ion currents used)
Option 3
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using predetermined response factors and characteristic ions)
• Qualitative analysis of each nondesignated POHC with a peak height >10% of the peak height of nearest inernal standard
• Quantitative analysis using calibration standards of nondesignated POHCs (using calculated response factors and characteristic ions)
Special Studies by GC/MS, GC/MS/SIM, HRMS
• Add appropriate internal standards
• Perform desired analysis, i.e.,
—dioxin cogener group analysis
—furan cogener group analysis
—specific analysis for 2,3,7,8-TCDD
—other
Decision Tree Code
Tier 1B
Tier 2B
Tier 3B
Tier 4B
Tier 5B

Figure II-4. Proposed semivolatiles screening protocol for POHCs and PICs from combustion sources.

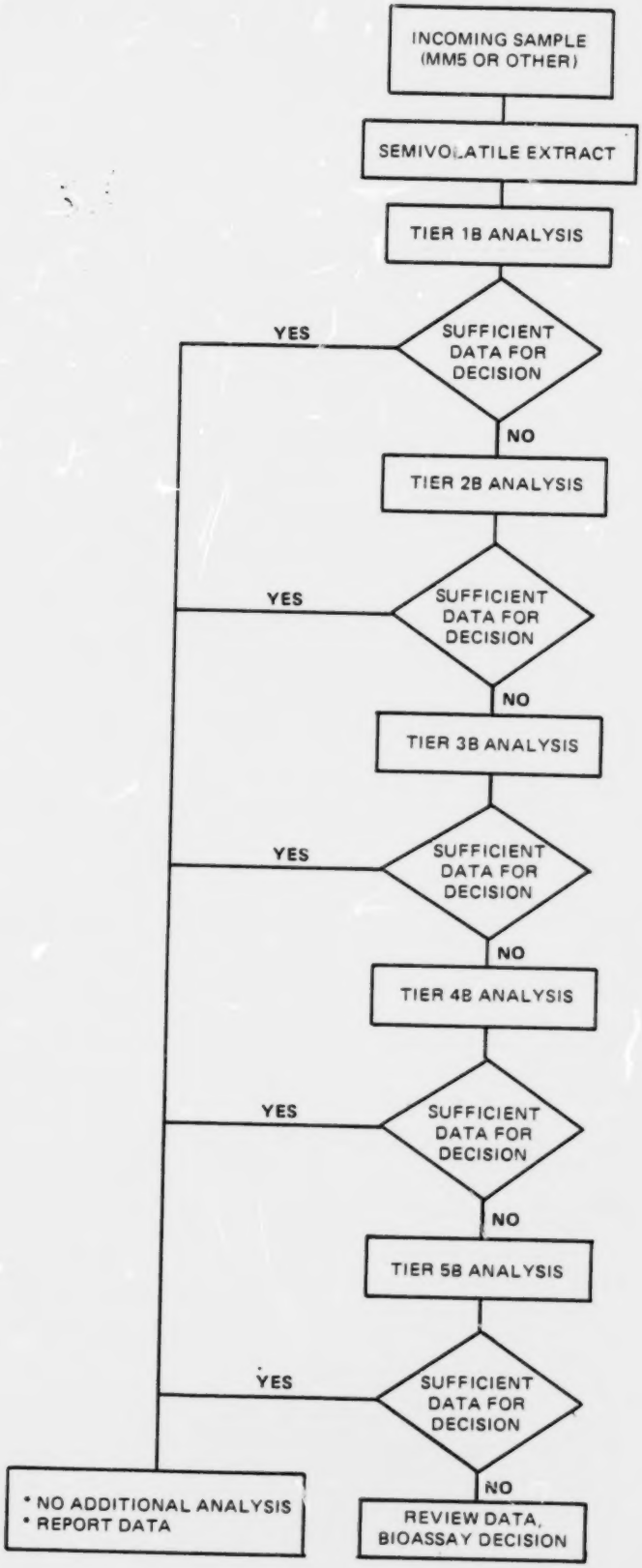

Figure II-5. Decision tree for semivolatiles.

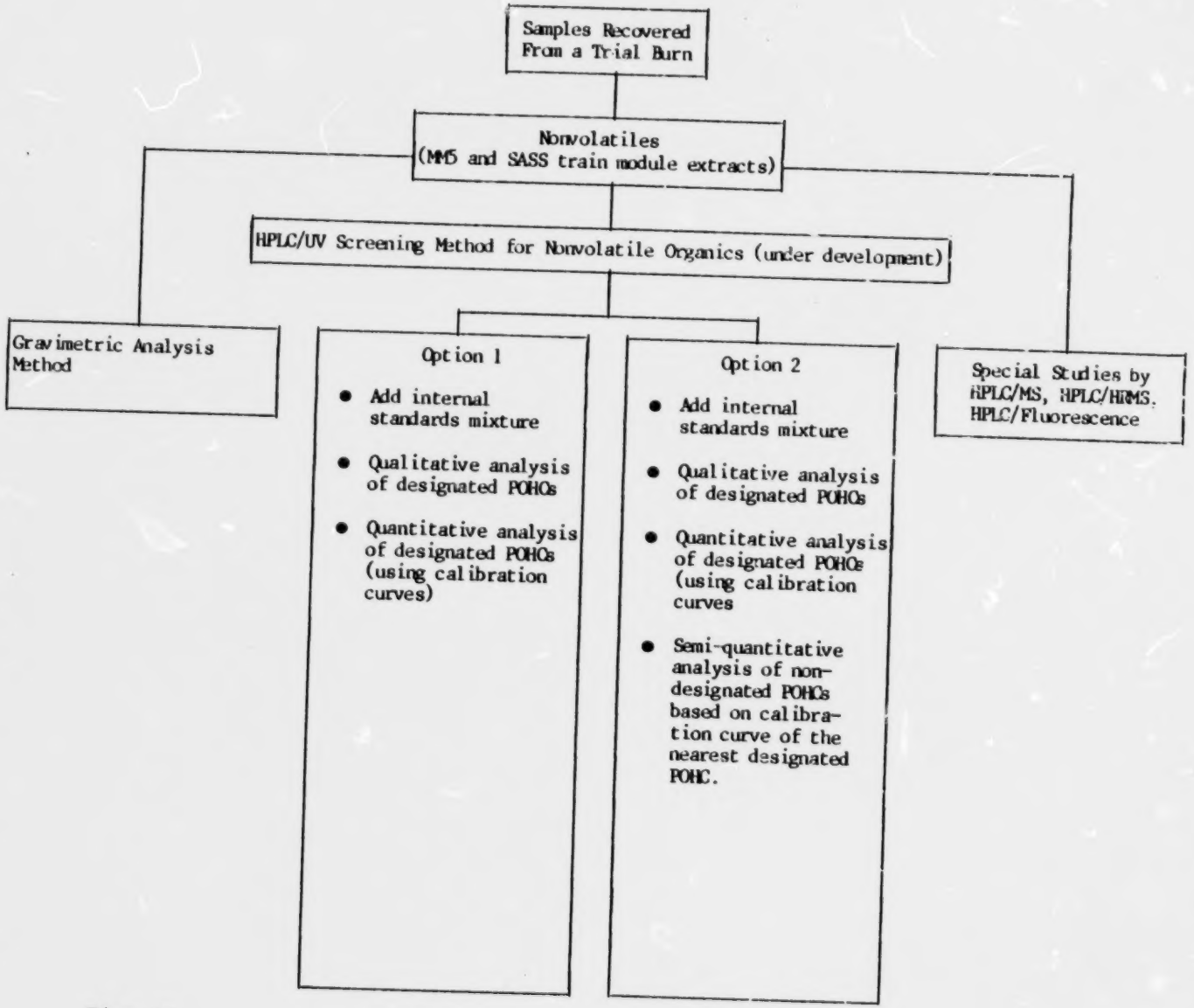
Samples Recovered From a Trial Burn
Nonvolatiles (MM5 and SASS train module extracts)
HPLC/UV Screening Method for Nonvolatile Organics (under development)
Gravimetric Analysis Method
Option 1
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using calibration curves)
Option 2
• Add internal standards mixture
• Qualitative analysis of designated POHCs
• Quantitative analysis of designated POHCs (using calibration curves
• Semi-quantitative analysis of non-designated POHCs based on calibration curve of the nearest designated POHC.
Special Studies by HPLC/MS, HPLC/HRMS, HPLC/Fluorescence
Decision Tree Code
Tier 1C
Tier 2C
Tier 3C
Tier 4C

Figure II-6. Proposed nonvolatiles screening protocol for POHCs and PICs from combustion sources.

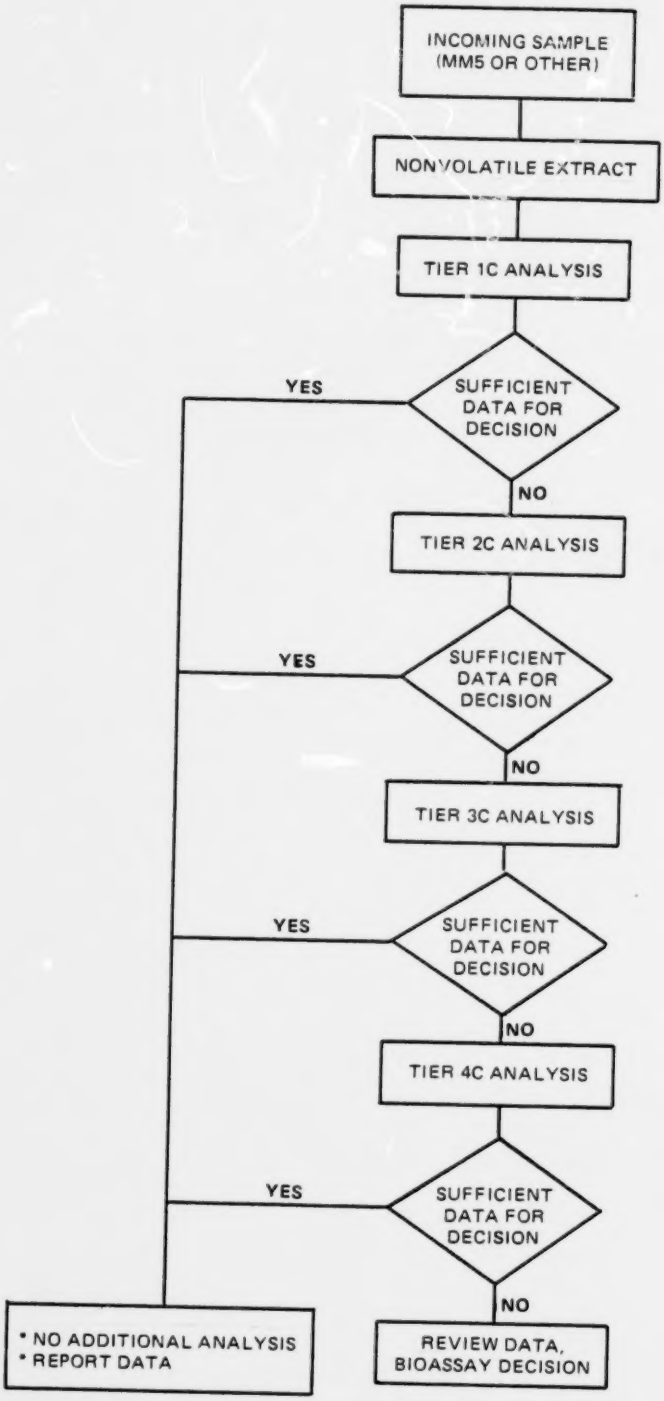

Figure II-7. Decision tree for nonvolatiles.

III. ANALYTICAL PROCEDURES

GC/FID SCREENING PROTOCOL FOR VOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Scope: This method covers the screening of volatile organic compounds collected on Tenax-GC/charcoal sorbent cartridges using a Volatile Organic Sampling Train (VOST). Because the majority of gas streams from incinerators sampled using VOST will contain a high concentration of water, the screening method is based on the quantitative thermal desorption of volatile organics from the sorbent traps and analysis by purge-and-trap GC/FID. For the purpose of definition, volatile organics are those compounds with boiling points less than 150 °C.

1.2 Range of sensitivity: The range of sensitivity of this procedure, defined as the slope of a plot of area response versus concentration, is dependent on the gas chromatograph, flame-ionization detector, and column used.

The upper limit of the range is dependent on the column capacity. The upper limit can be extended by collecting a smaller sample size or by splitting off part of the sample prior to the purge-and-trap apparatus.

The lower limit of the range is determined by the minimum detectable amount of the compound or compounds of interest.

1.3 Precision: Duplicate results by the same analyst should not differ by more than 25%.

1.4 Qualifications of Personnel: This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap equipment and gas chromatographs with FID detectors.

2.0 SUMMARY OF METHOD

The contents of sorbent cartridges from a VOST are thermally desorbed for 10 min at 180 °C with organic-free helium or nitrogen at a flow rate of 40 mL/min, bubbled through 5 mL of organic free water, and trapped on an analytical sorbent trap in a purge and trap apparatus. When desorption of the VOST cartridge is complete, the flow to the analytical trap is reversed and the cartridge is rapidly heated to 180 °C. The effluent flow from the trap is directed into the GC/FID. The volatile organic compounds are separated by temperature-programmed gas chromatography and detected by flame ionization. The concentration of volatile organics is then estimated.

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the end seals on VOST cartridges. A field blank should be carried through the sampling and handling protocol. This can serve as a check on such contamination.

3.2 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a blank to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.3 The laboratory where the analyses are performed should be completely free of solvents.

3.4 Impurities in the purge gas and from organics out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination.

4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit: The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater or equivalent) should be capable of heating the tubes to 180 ± 10 °C with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.2.1 Sample purger: The purging chamber should be designed to accept 5 mL of reagent-grade water with a water column at least 3 cm deep. The gaseous headspace between the water column and the analytical trap must have a total volume of less than 15 mL. The purge gas line from the thermal desorption unit should also have a total volume of less than 15 mL.

4.2.2 Trap: The analytical trap must be at least 25 cm long and have an inside diameter of at least 2.6 mm. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of Tenax-GC, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap. If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35 °C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

Before initial use, the trap should be conditioned overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180 °C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.2.3 Thermal desorber: The desorber should be capable of rapidly heating the analytical trap to 180 °C for desorption of the components of interest into the gas chromatograph.

4.3 Gas chromatograph: The gas chromatograph is an analytical system complete with a temperature-programmable gas chromatograpic oven, a flame ionization detector (FID), and all the required accessories including syringes, analytical columns, and gases.

4.3.1 Packed GC column: 1.8-m x 0.2-mm-ID glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.3.2 Megabore capillary column: 30-m x 0.53-mm-ID, coated with a 3-µm film of DB-624 (J&W Scientific) or equivalent).

4.4 Analytical trap packing materials:

4.4.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.4.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.4.3 Silica gel: 35/60 mesh.

4.4.4 Coconut charcoal: 35/60 mesh.

5.0 ANALYSIS PROCEDURE

5.1 Standard solutions

5.1.1 Stock solutions: Stock solutions of 1,2-dichloroethane, toluene, and p-xylene may be prepared from pure standard materials or purchased as certified solutions. To prepare stock solutions from pure chemicals, place about 9.8 mL of methanol in a 10-mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg. Using a 100-µL syringe, add several drops of the reference material to the flask, then reweigh. The liquid drops should fall directly into the methanol without contacting the neck of the flask. Dilute to a total volume of 10 mL with methanol. Calculate the concentration of the stock standards in ng/µL.

5.1.2 Calibration standard solutions: Using the stock standards, prepare a series of calibration standards in methanol containing 10, 50, and 100 ng/µL each of 1,2-dichloroethane, toluene, and p-xylene.

5.2 Calibration tubes: Calibration tubes are prepared by spiking blank Tenax or Tenax/charcoal VOST traps with 1 µL of the calibration standard solutions. The glass traps containing the sorbent material should be attached to the injection port of a gas chromatograph while maintaining the injection port temperature at 160 °C. Carrier gas flow through the traps should be set at about 50 mL/min. After directing the gas flow through the trap, 1 µL of a calibration standard solution is slowly injected through the GC injector port over about 15 sec. After about 30 sec, the gas flow to the trap should be shut off, the syringe removed, and the trap analyzed by purge-and-trap GC/FID.

5.3 Initial system calibration

5.3.1 Interface the thermal desorption unit, the purge-and-trap device, and the GC/FID to each other as instructed by the manufacturer.

5.3.2 GC/FID operating conditions

	Packed	Megabore
Initial column temperature	45 °C	10 °C
Initial column hold time	3 min	5 min
Column temperature program	8 °C/min	6 °C/min
Final column temperature	220 °C	160 °C
Final column holding time	15 min	5 min
Injector temperature	≈200 °C	≈200 °C
Carrier gas	helium at 30-40 mL/min	helium at 15 mL/min
FID gas flows	as per manufacturer's instructions	as per manufacturer's instructions

5.3.3 Calibration standards analysis: Adjust the purge gas flow rate to 40 mL/min on the purge-and-trap device. Add 5.0 mL of reagent grade water to the purging device. Place a prepared calibration sorbent cartridge in the thermal desorption apparatus. Desorb the standard components into the purge-and-trap system by heating the trap to 180 °C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. The standard compounds are then thermally desorbed from the analytical sorbent trap into the GC/FID. The analytical adsorbent trap is rapidly heated to 180 °C and its contents backflushed into the GC column with 15-40 mL/min of

helium. The GC column is then temperature programmed and the components eluting from the column detected using a flame ionization detector.

6.0 SAMPLE ANALYSIS

Samples are screened using the same analysis procedure as outlined in Section 5.3 for initial system calibration. Also, a field blank should be analyzed for each sampling site.

7.0 CALCULATIONS

7.1 A calibration curve is constructed by fitting a linear regression equation to the results of the analysis of calibration standards. The following equation is used:

$$A_i = M(C_i) + B$$

where:

A_i = FID area response summed for all standard compounds.

C_i = Total concentration of all standard compounds.

M = Slope of the line.

B = Intercept of line.

A correlation coefficient of greater than 0.97 must be obtained.

7.2 The concentration of the field blank and sample extracts are determined by summing the FID area responses for all detected peaks. The estimated concentration of volatile organics in the sample can be calculated using the equation given in Section 7.1.

7.3 Corrected sample extract concentrations are determined using the following equation:

$$C_{corrected} = C_{measured} - C_{blank}$$

Results of the analysis should be reported in the appropriate units.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method should operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest.

8.2 Before performing any analysis, the analytical system must be demonstrated to be free of interferences. This is accomplished by analyzing a blank Tenax or Tenax/charcoal sorbent cartridge.

8.3 The analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. Duplicate analysis by the same analyst should agree within 25%.

9.0 REFERENCES

9.1 Hansen, E.M., Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA-600/8-84-007, NTIS No. PB84-170042, March 1984.

9.2 Logan, T.J. et al., Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes 1 and 2. EPA-600/4-86-014a and b, NTIS No. PB86-145547 and PB86-145554, January 1986.

9.3 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., Method 5040, NTIS No. PB88-239223, February 1987.

GC/MS SCREENING METHOD FOR VOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Scope: This method covers the determination of volatile Principal Organic Hazardous Constituents (POHCs) and other volatile organic compounds, collected on Tenax and Tenax/charcoal sorbent cartridges using a Volatile Organic Sampling Train (VOST). Since the majority of gas streams sampled using VOST contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile organic compounds from the sorbent cartridges and analysis by purge-and-trap GC/MS.

1.2 Sensitivity: The sensitivity of the analytical method for a particular volatile organic compound depends on the level of interferences and the presence of detectable levels of that specific compound in blanks. The desired analytical detection limit is ≈20 ng for a particular compound desorbed from the sorbent traps. The upper limit of the range of sensitivity is dependent on the column capacity. The upper limit can be extended by collecting a smaller sample size or by splitting off part of the sample prior to the purge and trap apparatus.

1.3 Precision: Duplicate results by the same analyst should not differ by more than 25%.

1.4 Qualifications of personnel: This method is restricted to use by experienced mass spectroscopists or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

The contents of sorbent cartridges are spiked with internal standards and thermally desorbed for 10 min at 180 °C with organic-free helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free water, and trapped on an analytical adsorbent trap. After the 10-min desorption, the analytical adsorbent trap is rapidly heated to 180 °C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile organic compounds are separated by temperature-programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of the volatile organic compounds are calculated using the internal standard technique.

3.0 INTERFERENCES

3.1 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the end seals on VOST cartridges. A field blank should be carried through the sampling and handling protocol. This can serve as a check on such contamination.

3.2 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a blank to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.3 The laboratory where the analyses are performed should be completely free of solvents.

3.4 Impurities in the purge gas and from organics outgasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.

4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit: The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater or equivalent) should be capable of thermally desorbing the VOST sorbent tubes. It should be capable of heating the tubes to 180 ± 10 °C with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.2.1 Sample purger: The purging chamber should be designed to accept 5 mL of reagent grade water with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas line from the thermal desorption unit should have a total volume of less than 15 mL.

4.2.2 Trap: The analytical trap must be at least 25 cm long and have an inside diameter of at least 2.6 mm. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of Tenax-GC, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap. If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35 °C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180 °C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.2.3 Thermal desorber: The desorber should be capable of rapidly heating the trap to 180 °C for desorption of the components of interest into the GC/MS.

4.3 Gas Chromatograph/Mass Spectrometer System:

4.3.1 Gas chromatograph: A gas chromatograph is an analytical system complete with a temperature programmable gas chromatographic oven and all required accessories including syringes, analytical columns, and gases.

4.3.1.1 Packed GC column: 1.8-m x 0.2-mm I.D. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.3.1.2 Mega-bore capillary column: 30 m long x 0.53 mm I.D., coated with a 3 µm film of DB-624. (J&W Scientific or equivalent)

4.3.2 Mass spectrometer: Capable of scanning from 35-260 amu every 3 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table III-B-1 when a 50 ng injection of 4-bromofluorobenzene (BFB) is made into the gas chromatograph inlet.

4.3.3 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the designated POHCs and achieves all acceptable performance criteria (see Table 1) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.3.4 Data system: A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot i defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.4 Analytical trap packing materials:

4.4.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.4.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.4.3 Silica gel: 35/60 mesh.

4.4.4 Coconut charcoal: 35/60 mesh.

5.0 REAGENTS

5.1 Stock solutions: Stock solutions of designated POHCs may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.1.1 Place about 9.8 mL of methanol in a 10-mL tared volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.1.2 Add the assayed reference material, as described below.

5.1.2.1 Liquids: Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.1.2.2 Gases: To prepare standards for any compounds that boil below 30 °C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the pure reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.1.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.4 Transfer the stock standard solution into a Teflon-sealed screw cap bottle. Store, with minimal headspace, at -10 °C to -20 °C and protect from light.

5.1.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.2 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.3 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution of each internal standard should be prepared at a concentration of 25 µg/mL of each internal standard compound.

5.4 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 µg/mL of BFB in methanol should be prepared.

5.5 Calibration standards: Calibration standards for the designated POHCs at a minimum of five concentration levels (10, 25, 50, 75, and 100 ng/µL) should be prepared from the secondary dilution of stock standards (see Sections 5.1 and 5.2). Prepare these solutions in methanol. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. Store for one week only in a vial with no headspace.

5.6 Standard solution storage: Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10 °C to -20°C in screw-cap amber bottles with Teflon liners.

5.7 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.7.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.7.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.7.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 hr. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.8 Methanol: Pesticide quality or equivalent. Store apart from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected using the appropriate sampling method as specified in the approved site-test plan for an incinerator trial burn.

Generally, the sampling method used is from or is similar to a sampling method specified in Test Methods for Evaluating Solid Wastes, SW 846.

6.2 Sample obtained from a VOST should be analyzed within 2-6 weeks of collection.

7.0 ANALYSIS PROCEDURE

7.1 Calibration tubes: Calibration tubes containing designated POHCs are prepared by spiking a blank Tenax/charcoal trap with a 1 µL of the calibration standard solutions (including internal standards). The glass traps containing the sorbent material should be attached to the injection port of a gas chromatograph while maintaining the injector port temperature at 160 °C. Carrier gas flow through the traps should be set at about 50 mL/min after directing the gas flow through the trap, 1 µL of a calibration standard solution is slowly injected through the GC injector port over about 15 sec. After about 30 sec, the gas flow to the trap should be shut off, the syringe removed, and the trap analyzed by purge-and-trap GC/MS.

7.2 Initial system calibration:

7.2.1 Interface the thermal desorption unit, the purge-and-trap device, and the GC/MS to each other as instructed by the manufacturer.

7.2.2 Recommended GC/MS operating conditions

Electron energy: 70 volts (nominal).

Mass range: 35-260 amu.

Scan time: Set to give a minimum of 5 scans/peak but not to exceed 7 sec/scan.

Source temperature: As per manufacturer's specifications.

	Packed	Megabore
Initial column temperature	45 °C	10 °C
Initial column hold time	3 min	5 min
Column temperature program	8 °C/min	6 °C/min
Final column temperature	220 °C	160 °C
Final column holding time	15 min	5 min
Injector temperature	≈200 °C	≈200 °C
Carrier gas	helium at 30-40 mL/min	helium at 15 mL/min

Table III-B-1. BFB Key Ion Abundance Criteria

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

7.2.3 Each GC/MS system must be hardware-tuned to meet the criteria in Table III-B-1 for a 50-ng injection or purging of 4-bromofluorobenzene (2-μL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.4 Condition the analytical trap in the purge-and-trap device overnight at 180 °C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180 °C with the column at 220 °C.

7.2.5 Initial calibration for designated POHCs

7.2.5.1 Analytical procedures: Adjust the purge gas flow rate to 40 mL/min on the purge-and-trap device. Add 5.0 mL of reagent grade water to the purging device. Place a sorbent cartridge prepared in Section 7.1 in the thermal desorption apparatus and desorb it into the purge-and-trap system by heating the trap to 180 °C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10 min desorbing period, the compounds are thermally desorbed from the analytical sorbent trap into the GC/MS. The analytical adsorbent trap is rapidly heated to 180 °C and its contents backflushed into the GC column with 15-40 mL/min of helium. The GC column is then temperature programmed and the components eluting from the column are detected by mass spectrometry.

7.2.5.2 Determination of response factors: Tabulate the area of the primary characteristic ion against concentration for each designated POHC. Calculate response factors (RFs) for each designated POHC as follows:

$$RF = (A_p C_{IS})/(A_{IS} C_p)$$

where:

A_p = Area of the characteristic ion for a designated POHC being measured.

A_{IS} = Area of the characteristic ion for a specific internal standard.

C_p = Concentration (ng) of the designated POHC being measured.

C_{IS} = Concentration (ng) of a specific internal standard.

7.2.5.3 An average response factor (RF_{avg}) should be calculated for each designated POHC. The percent relative standard deviation should also be calculated for each designated POHC using the following equation:

$$\% \text{ RSD} = 100 \left[\frac{\text{standard deviation}}{RF_{avg}}\right]$$

The % RSD for each designated POHC must be less than 25%.

7.3 Continuing calibration check: A continuing calibration check should be performed every 12 hrs. This is accomplished by analyzing the calibration solution containing 50 ng/μL of each designated POHC. The calculated response factors for the designated POHCs are compared to the average response factors of the initial calibration. The difference should be less than 25%. If values greater than 25% are obtained, corrective action must be taken. Also, the relative retention times of each designated POHC in each calibration run should agree within 0.06 relative retention time units. If the retention time for any internal standard changes by more than 30 sec from the last calibration check, the chromatographic system must be inspected for malfunctions and corrections made. If the EICP area for any internal standard changes by a factor of two (-50% to +100%) from the last daily continuing calibration check, the GC/MS system must be inspected for malfunctions and corrective action taken.

7.4 Sample analysis:

7.4.1 It is recommended that if enough sorbent cartridges are available, that one cartridge be screened by GC/FID screening protocol. This will help minimize contamination of the GC/MS system from samples containing high concentrations of organic compounds.

7.4.2 Spike sorbent cartridges with 50 ng of each internal standard using the procedure outlined in Section 7.1 for preparation of calibration tubes.

7.4.3 Adjust the purge gas flow rate to 40 mL/min on the purge-and-trap device. Add 5.0 mL of reagent grade water to the purging device. Place the sorbent cartridge in the thermal desorption apparatus and desorb it into the purge-and-trap system by heating the trap to 180 °C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10 min desorbing period, the compounds are thermally desorbed from the analytical sorbent trap into the GC/MS. The analytical adsorbent trap is rapidly heated to 180 °C and its contents backflushed into the GC column with 15-40 mL/min of helium. The GC column is then temperature programmed and the components eluting from the column are detected by mass spectrometry. Samples should be analyzed using the GC/MS operating conditions outlined in Section 7.2.2.

7.4.4 Perform all qualitative and quantitative data interpretations as specified in Section 8 of the procedure.

8.0 QUALITATIVE AND QUANTITATIVE DATA INTERPRETATION

Table III-B-2 summarizes the data interpretation options outlined in this procedure. Each option is discussed in detail below.

8.1 Option 1:

8.1.1 Qualitative analysis:

8.1.1.1 An analyte (i.e., designated POHC) is identified by comparison of the sample mass spectrum with a reference mass spectrum of a standard of the suspected designated POHC. The reference mass spectrum should be obtained on the user's GC/MS within the same 12 hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from one of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC; and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

8.1.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12 hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the POHC of interest.

8.1.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

8.1.1.4 The relative intensities of ions specified in Paragraph 8.1.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)

8.1.2 Quantitative analysis

8.1.2.1 When a designated POHC has been identified, quantitation of that POHC will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

8.1.2.2 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})}{(A_{IS})\ (RF)}$$

Table III-B-2. Data Interpretation Options

Option	Designated POHC		Non-designated POHC	
	Qualitative	Quantitative	Qualitative	Quantitative
1	yes	yes	no	no
2	yes	yes	yes	semi-quantitative
3	yes	yes	yes	yes

where:

A_x = Area of the characteristic ion of the designated POHC measured.

I_{IS} = Amount of internal standard injected (ng).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

8.2 Option 2

8.2.1 Qualitative analysis

8.2.1.1 Designated POHCs:

8.2.1.1.1 An analyte (e.g. designated POHC) is identified by comparison of the sample mass spectrum with a reference mass spectrum of a standard of the suspected designated POHC. The reference mass spectrum should be obtained on the user's GC/MS within the same 12-hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from one of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC; and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

8.2.1.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12-hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the POHC of interest.

8.2.1.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

8.2.1.1.4 The relative intensities of ions specified in Paragraph 8.2.1.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 %.)

8.2.1.2 Non-designated POHCs:

8.2.1.2.1 For samples containing components which are not designated POHCs, a library search may be made for the purpose of tentative identification. All non-designated POHC peaks which have peak heights greater than 10% of the peak height of the nearest internal standard should be searched. Computer-generated library routines should not use normalization routines that would misrepresent the library or unknown spectra

when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.)

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

8.2.2 Quantitative analysis

8.2.2.1 Designated PLHC

8.2.2.1.1 When a designated POHC has been identified, the quantitation of that POHC will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

8.2.2.1.2 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})}{(A_{IS})\ (RF)}$$

where:

A_x = Area of the characteristic ion of the designated POHC being measured.

I_{IS} = Amount of internal standard injected (ng).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

8.2.2.2 Non-designated POHCs

8.2.2.2.1 Estimation of the concentration of compounds which are not designated POHCs can be made. The following equation (which is similar to the equation in paragraph 8.2.2.1.2) is used:

$$\text{Estimated weight (ng)} = \frac{(A_x)\ (I_{IS})}{(A_{IS})\ (RF)}$$

where:

A_x = Area from the total ion-current of the compound of interest

I_{IS} = Amount of internal standard injected (ng).

A_{IS} = Area from the total ion-current of the internal standard.

RF = Assumed to be 1.

8.3 Option 3

8.3.1 Qualitative analysis

8.3.1.1 Designated POHCs:

8.3.1.1.1 An analyte (e.g., designated POHC) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected designated POHC. Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12-hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from calibration standards. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC; and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

8.3.1.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12-hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the POHC of interest.

8.3.1.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

8.3.1.1.4 The relative intensities of ions specified in Paragraph 8.3.1.1.3 must agree within plus or minus 20% between the standard and

sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

8.3.1.2 Non-designated POHCs:

8.3.1.2.1 For samples containing components which are not designated POHCs, a library search may be made for the purpose of tentative identification. All non-designated POHC peaks which have peak heights greater than 10% of the peak height of the nearest internal standard should be searched. Computer-generated library routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

8.3.2 Quantitative analysis

8.3.2.1 Designated POHC

8.3.2.1.1 When a designated POHC has been identified, the quantitation of that POHC will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

8.3.2.1.2 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})}{(A_{IS})\ (RF)}$$

where:

A_x = Area of the characteristic ion of the designated POHC being measured.

I_{IS} = Amount of internal standard injected, (ng).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

8.3.2.2 Non-designated POHCs

8.3.2.2.1 For the quantitation of non-designated POHCs, prepare a series of calibration standards corresponding to 10, 25, 50, 75, and 100 ng/μL in methanol. Add the proper amount of internal standard solution to each mixture to yield an internal standard concentration equal to 50 ng per sorbent cartridge. Prepare calibration tubes as specified in Section 7.1 and analyze the standards using the GC/MS condition given in Section 8.0.

8.3.2.2.2 Calculate response factors (RFs) for each non-designated POHC as follows:

$$RF = \frac{(A_N\ C_{IS})}{(A_{IS}\ C_N)}$$

where:

A_N = Area of the characteristic ion for the non-designated POHC being measured.

A_{IS} = Area of the characteristic ion for the internal standard.

C_{IS} = Concentration (ng) of the internal standard.

C_N = Concentration (ng) of the non-designated POHC being measured.

8.3.2.2.3 The total weight in nanograms of a non-designated POHC present in a sample can be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})}{(A_{IS})\ (RF)}$$

where:

A_x = Area of the characteristic ion of the designated POHC being measured.

I_{IS} = Amount of internal standard injected, (ng).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses these methods should operate a formal quality control program. The minimum requirement of this program should consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples. When results of sample spikes indicate atypical method performance, a QC check standard (50 ng designated POHC calibration standard) must be analyzed to verify that the measurements were performed in an in-control mode of operation.

9.2 Before processing any samples, the analyst should demonstrate, through the analysis of a blank sorbent cartridge and reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed, a laboratory blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

9.3 Each day that analyses are performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Two questions should be asked concerning the calibration standard: do the peaks look normal and is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate if the column is still good, if the gas lines are contaminated, or a gas leak has developed. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. If any changes are made to the system (e.g., column changed), the system must be recalibrated.

9.4 Required instrument QC is found in the following sections of this method:

9.4.1 The GC/MS system must be tuned to meet BFB tuning criteria as specified in Section 4.3.2 and 7.2.3.

9.4.2 There must be an initial calibration of the GC/MS system for the designated POHCs as specified in Section 7.2.5.

9.4.3 A continuing calibration check must be carried out at least once every 12 hrs as specified in Section 7.3.

10.0 REFERENCES

10.1 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., Method 8240, NTIS No. PB88-239223, February 1987.

10.2 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., Method 5040, NTIS No. PB88-239223, February 1987.

10.3 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.

10.4 Provost, L.P. and Elder, R.S., "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

10.5 Eichelberger, J.W.; Harris, L.E.; and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

10.6 Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

SOXHLET EXTRACTION METHOD FOR SOLID SORBENT MODULES

1.0 SCOPE AND APPLICATION

1.1 The procedure is for extracting nonvolatile and semivolatile organic compounds from XAD resins or other solid adsorbents.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics.

2.0 SUMMARY OF METHOD

2.1 A sample is placed in an extraction thimble, spiked with surrogate standards, and extracted with methylene chloride for 16 hrs in a Soxhlet Extractor. The extract is then dried and concentrated to the appropriate final volume.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the sample will vary considerably from one incineration source to another.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastic containers should be avoided.

3.4 Soap residues left on improperly cleaned glassware may cause degradation of certain analytes. Many organophosphorus pesticides will degrade in this situation.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40-mm ID, with 500-mL round-bottom flask, extraction thimbles, and appropriate rheostat-controlled heating mantle.

4.2 Drying column - 20-mm-ID Pyrex chromatographic column with Pyrex glass wool at the bottom and a Teflon stopcock.

4.3 Kuderna-Danish (K-D) apparatus:

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent).

4.3.3 Snyder columns - Three-ball macro (Kontes K-503000-0121 or equivalent) and two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Water bath - Heated, with concentric ring cover and temperature control of ±5 °C.

4.5 Volumetric pipet - Class A (1 mL)

5.0 REAGENTS

5.1 Sodium sulfate - (ACS) granular anhydrous (purified by washing with methylene chloride followed by heating at 400 °C for 4 hrs in a shallow tray).

5.2 Methylene chloride - "Distilled-in-glass" or equivalent grade.

5.3 Methanol - "Distilled-in-glass" or equivalent grade.

5.4 Surrogate standards - A surrogate standard (i.e., a chemically inert compound which is not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to sample extraction. The recovery of the surrogate is used to monitor matrix effects and gross sample processing errors. Recommended surrogate standards for base/neutral and acid groups in general are given below. However, if a specific class of compounds is to be investigated, other compounds which better correspond to that class may be used as surrogates.

5.4.1 Base/neutral and acid surrogate spiking solution: The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.4.1.1 Prepare a surrogate standard spiking solution in 10% methanol/90% methylene chloride that contains 100 µg/mL of the base/neutral surrogates and 200 µg/mL of the acid surrogates. The concentration of these standards can be varied as necessary.

6.0 SAMPLE COLLECTION AND PRESERVATION

6.1 Samples should be collected using the appropriate sampling method as specified in the approved site-test plan for the incinerator trial burn.

7.0 SAMPLE HANDLING

7.1 Remove the XAD resin (or other adsorbent if different from XAD) from the sorbent module and place in an extraction thimble. Rinse the sorbent module and glass wool plugs with the extraction solvent and add the rinse to the extraction flask. Add 1.0 mL of the surrogate standard spiking solution onto the sample.

7.2 Place 300 mL of the extraction solvent into a 500-mL round bottom flask containing several clean boiling chips. Attach the flask to the Soxhlet extractor and extract the sample for ≈16 hr. The extraction rate should be adjusted to yield 5 to 6 solvent exchanges per hour during Soxhlet extraction.

7.3 Allow the extract to cool to ambient temperature after the extraction is complete.

7.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.5 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract into the K-D concentrator assembled in Section 7.4. Rinse the extractor flask and sodium sulfate column with 100-125 mL of methylene chloride to complete the quantitative transfer.

7.6 Add several clean boiling chips to the flask and attach a 3-ball Snyder column. Prewet the Synder column by adding about 1-2 mL of methylene chloride to the top of the column. Place the K-D apparatus on a water bath containing 55-60 °C water so that the concentrator tube is partially immersed in the hot water and the lower rounded surface of the flask is bathed with warm vapors. Adjust the position of the apparatus and the water temperature to complete the concentrations of the sample in approximately 20 min. When the apparent volume reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.7 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with several milliliters of methylene chloride. Adjust the final volume of the extract to 10.0 mL with methylene chloride.

7.8 Submit 1 to 5 µL of the extract to the Total Chromatographable Organics (TCO) protocol. If further concentration is indicated, proceed to paragraph 7.9. If no further concentration is required, skip to paragraph 7.10.

7.9 If further concentration is indicated by the TCO protocol, add a clean boiling chip to the concentrator tube and attach a two-ball micro Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of

the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature to complete the concentration in about 10 min. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Synder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL as necessary with methylene chloride.

7.10 The extracts obtained may now be analyzed for analyte content using the appropriate analysis method for semivolatile and/or nonvolatile organic constituents.

8.0 EXTRACT STORAGE

Extracts should be stored in Teflon-sealed capped vials and labeled properly. The extracts should be stored at 4 °C until analyzed.

9.0 QUALITY CONTROL

9.1 A reagent blank should be subjected to exactly the same analytical procedures as those used on actual samples.

10.0 REFERENCES

10.1 40 CFR part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

10.2 Test Methods for Evaluating Solid Waste, SE 846, 3rd ed., NTIS No. PB88-239223, Method 3540 (Soxhlet Extraction), February 1987.

SCREENING PROCEDURE FOR TOTAL CHROMATOGRAPHABLE ORGANICS (TCO)

1.0 APPLICABILITY AND PRINCIPLE

1.1 Scope: This method provides semi-quantitative data on the levels of organic compounds with boiling points between 100 °C and 300 °C collected on and extracted from SASS or MM5 train sorbent modules.

This method is based on separation and detection of the components of the extract using gas chromatography with flame ionization detection.

1.2 Range of sensitivity: The range of sensitivity of this procedure, defined as the slope of a plot of area response versus concentration, is dependent on the gas chromatograph and column used. The range of sensitivity should be verified regularly.

The upper limit of the range is dependent on column capacity and detector nonlinearity. The upper limit can be extended by dilution of sample extracts with methylene chloride.

The lower limit of the range is determined by the minimum detectable concentration of standards. The minimum detectable limit is defined as 5 times the signal-to-noise ratio.

1.3 Precision: Duplicate results by the same analyst should not differ by more than 15%.

1.4 Accuracy: The results of a quality control standard, run daily, should be considered deficient if it differs by more than 15% from the initial calibration value.

If the value falls outside the accepted range, corrective action must be taken and the quality control standard must be reanalyzed. If the second value is still outside the acceptable limits, a new calibration curve should be run.

2.0 SUMMARY OF METHOD

2.1 Methylene chloride extracts of the sorbent modules are concentrated to a final volume of 10 mL. A 1- to 5-μL aliquot of a methylene chloride extract is injected into a gas chromatograph and analyzed. Integration of detector response begins at the elution time for n-heptane (boiling point ≈98 °C) and terminates at the retention time of n-heptadecane (boiling point = 303 °C). The integrated area covers organic materials with boiling points in the 100 to 300 °C range.

Standards are prepared to cover the linear working range of the analytical system. A calibration curve is made of the total integrator response versus concentration.

The corresponding TCO value for a sample is then determined from the calibration curve.

3.0 DEFINITIONS

TCO: Total Chromatographable Organics

SASS: Source Assessment Sampling System

MM5: Modified Method 5

°C: degrees centigrade

min: minutes

FID: Flame ionization detector

m: meters

mm: millimeters

C_7 through C_{17} n-Alkanes: heptane through heptadecane

mL: milliliter

µL: microliter

ID: inside diameter or internal diameter

µm: micrometer

4.0 INTERFERENCES

4.1 The analytical system must be demonstrated to be free from contaminants prior to any sample analysis. This is verified by running a quality control sample.

4.2 A reagent blank for each new batch of reagents must be analyzed to verify that reagents are contaminant free.

4.3 If duplicate runs of the same sample show increasing concentration (greater than 15%) or if cross contamination is suspected, a reagent blank must be run to verify that the analytical system is contamination free.

5.0 APPARATUS AND MATERIALS

5.1 Gas chromatograph: A gas chromatograph equipped with an FID and a linear temperature programmer. An integrator must be interfaced with the detector to measure peak areas.

5.2 Gases:

5.2.1 Helium: Zero grade or better.

5.2.2 Air: Zero grade or better.

5.2.3 Hydrogen: Zero grade or better.

5.3 Syringe - 10-µL syringe (Hamilton 701N or equivalent).

5.4 Septa - Septa should exhibit low bleed characteristics during temperature programming.

5.5 Columns:

5.5.1 Packed column: 1.8-m x 0.2-mm outside diameter stainless steel column of 10% OV-101 (or other methyl silicone phase) on 100/120 mesh Supelcoport.

5.5.2 Capillary column - 30-m x 0.32-mm ID bonded-phase fused-silica capillary column with a 1.0 micron film thickness (J&W DB-5 or equivalent).

6.0 REAGENTS AND STANDARD

6.1 Methylene chloride - "Distilled-in-Glass" or "Nanograde" or equivalent purity.

6.2 C_7-, C_{10}-, C_{12}-, C_{14}-, and C_{17}-n-alkanes - Minimum purity of greater than 99 percent.

7.0 SAMPLE HANDLING AND PRESERVATION

7.1 Extracts are prepared as specified in the protocol entitled "Soxhlet Extraction Method for Solid Sorbent Modules." A 1- to 5-µL aliquot of the extract is analyzed using the conditions given in Section 8 of this protocol.

7.2 Extracts should be stored in a refrigerator at or below 4 °C. This helps minimize analyte degradation. Extracts should be analyzed as soon as possible after sample receipt and preparation to minimize loss of analytes due to volatilization or degradation.

8.0 ANALYSIS PROCEDURE

8.1 GC operating conditions: Two gas chromatographic methods are acceptable for TCO analysis. These include capillary column and packed column methods. General operating conditions for the two methods are listed in Sections 8.1.1 and 8.1.2; however, minor adjustments may be necessary to optimize the analysis for a specific analytical system.

8.1.1 Capillary column GC operating conditions

Column - J&W DB-5 fused silica capillary column, 30-m x 0.32-mm ID with a 1.0 µm film thickness or equivalent.

Temperature program - 40 °C held for 4 min, then programmed to 300 °C at 20 °C/min, and hold until all compounds elute.

Carrier gas - 1-2 mL/min of helium.

Injector temperature - 290 °C.

Detector - FID at 325 °C.

Injection mode - 1 - 2 µL splitless with a 45-sec vent delay.

8.1.2 Packed column GC operating conditions

Column - 1.8-m x 0.2-mm stainless steel column containing 10% OV-101 on 100/120 mesh Supelcoport or equivalent.

Temperature program - 50 °C held for 5 min, then programmed to 250 °C at 20 °C/min, and held at 250 °C until all compounds elute.

Carrier gas - 30 mL/min of helium.

Injector temperature - 290 °C.

Detector - FID at 300 °C.

Injection volume - 1-5 µL.

8.2 Calibration

8.2.1 Standards preparation - Standards are prepared to cover the linear working range of the analytical system. A minimum of 5 standards are prepared to cover the range.

8.2.2 A stock standard solution is prepared by injecting 100 µL each of C_7, C_{10}, C_{12}, C_{14}, and C_{17} into a 10-mL volumetric flask and diluting to a total volume of 10 mL with dichloromethane. This stock solution will contain the following concentrations:

Compound	Concentration (mg/mL)
C_7	6.8
C_{10}	7.3
C_{12}	7.5
C_{14}	7.6
C_{17}	7.8

Serial dilutions of the stock solutions are made to cover the linear working range.

8.2.3 Standards are analyzed in duplicate using the conditions outlined in Section 7.1. Quantitative calibration of the TCO procedure is accomplished by summing the integrator response of C_{10}, C_{12}, and C_{14}. A calibration curve of total integrator response versus total concentration is obtained.

8.3 Sample analysis

8.3.1 A 1-5-µL aliquot of the sample extract is injected into a GC using the conditions given in Section 7.1. Peak areas over the TCO range window (C_7 through C_{17}) are summed, and a corresponding TCO value is calculated.

8.3.2 If the TCO value is outside the linear working range, the sample extract must be concentrated or diluted as needed, and reanalyzed.

8.3.3 A solvent blank treated in the same manner as a sample extract must also be analyzed. The solvent blank's TCO value should be subtracted from the TCO value for sample extracts.

8.4 Calculations

8.4.1 The calibration curve is constructed by fitting a linear regression equation to the results of the analysis of calibration standard solutions. The following equation is used:

$$A_i = M(C_i) + B \qquad (8.4\text{-}1)$$

where A_i = FID area response
C_i = concentration
M = slope of line
B = intercept of line

A correlation coefficient of greater than 0.97 must be obtained.

8.4.2 The concentration of the blank and sample extracts (both containing surrogate standards) are determined by summing the FID area response over the TCO retention time span and calculating the concentration from equation 8.4-1.

8.4.3 Corrected sample extract concentrations are determined using the following equation:

$$C_{corrected} = C_{measured} - C_{blank}$$

Results of the analysis should be reported in the appropriate units.

9.0 QUALITY CONTROL

9.1 A quality control standard must be run daily to verify the analytical systems performance. If the measured value falls outside the accepted range, corrective action must be taken.

9.2 Duplicate results by the same analyst should not differ by more than 15%.

9.3 The correlation coefficient for the calibration curve should be greater than 0.97.

10.0 REFERENCES

10.1 Lentzen, D.E. et al., "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," 2nd ed., EPA-600/7-78-201, NTIS No. PB293-795, October 1978.

10.2 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., NTIS No. PB88-239223, Method 0010, Appendix B, February 1987.

GC/MS SCREENING METHOD FOR SEMIVOLATILE ORGANIC COMPOUNDS

1.0 APPLICABILITY AND PRINCIPLE

1.1 Scope: This method may be used to determine the concentration of semivolatile organic compounds extracted from MM5 and SASS train modules. This method may be used to semiquantitate or quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a capillary GC column.

1.2 Range of sensitivity: The range of sensitivity of this procedure, defined as the slope of a plot of area response versus concentration, is dependent on the gas chromatograph, mass spectrometer, and capillary column used.

The upper limit of the range is dependent on column capacity. The upper limit can be extended by dilution of the sample extracts with methylene chloride.

The lower limit of the range is determined by the minimum detectable concentration of the analyte of interest which may be determined by using standard solutions. The minimum detectable amount is defined as 5x the signal-to-noise ratio. This lower limit may also be matrix dependent.

1.3 Precision: Duplicate results by the same analyst should not differ by more than 25%.

1.4 Accuracy: The results of a quality control standard, run daily, should be considered deficient if response factors differ by more than 25% from initial calibration values.

If a value falls outside the accepted range, corrective action must be taken and the quality control sample reanalyzed. If the second value is still outside the acceptable range, a new calibration curve should be run.

1.5 Qualifications of personnel: This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography/mass spectrometry equipment and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

Methylene chloride extracts of MM5 or SASS train samples are analyzed using capillary column GC/MS. Calibration curves are generated for the designated POHCs and the levels of the designated POHCs in the extracts are quantitated. Qualitative identification of major peaks, which are not designated POHCs, may also be done. Methods for semi-quantitation or quantitation of these compounds are given.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of an interferent is as a result of preparation and/or cleanup of the samples, and if so, take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur when high-level and low-level samples are sequentially analyzed. Whenever an unusually high-level sample is encountered, it should be followed by the analysis of a solvent blank to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - An analytical system equipped with a linear-temperature programmer and split/splitless and/or "on-column" injectors.

4.2 Capillary column - 30-m x 0.32-mm internal diameter, bonded-phase fused-silica capillary column with a 1.0-micron film thickness (J&W DB-5 or equivalent).

4.3 Mass spectrometer - Any mass spectrometer capable of scanning from 35 to 500 amu every 1 sec or less with unit resolution, using 70 eV electron energy in the electron-impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 50 ng of decafluorotriphenylphosine (DFTPP) which meets the tuning criteria outlined in Table III-E-1.

4.4 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 20 ng per injection for each compound of interest and achieves acceptable DFTPP tuning criteria may be used. A direct capillary or glass-lined "open split" interface is recommended.

4.5 Data system - A computer system must be interfaced to the mass spectrometer. The data system must allow for the continuous acquisition and storage of machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must be available that allows integration of the area abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should be available.

4.6 Syringes - 10-µL syringe (Hamilton 701N or equivalent).

4.7 Carrier gas - Zero-grade helium or better.

Table III-E-1. DFTPP Key Ion and Ion Abundance Criteria[a]

Mass	Ion abundance criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995 (1975).

5.0 REAGENTS AND STANDARDS

5.1 Methylene chloride - "Distilled-in-Glass" or "Nanograde" or equivalent purity.

5.2 Internal standards:

5.2.1 1,4-Dichlorobenzene-d_4: >99% purity

5.2.2 Naphthalene-d_8: >99% purity

5.2.3 Acenaphthene-d_{10}: >99% purity

5.2.4 Phenanthrene-d_{10}: >99% purity

5.2.5 Chrysene-d_{12}: >99% purity

5.2.6 Perylene-d_{12}: 99% purity

5.3 GC/MS tuning standard - The standard is a methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP). It should be stored at 4 °C or less when not being used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected using the appropriate sampling method as specified in the approved site test plan for the incinerator burn. Generally, the sampling methods are from or are similar to sampling methods specified in SW 846, Test Methods for Evaluating Solid Waste.

7.0 SAMPLE PREPARATION

7.1 Samples should be prepared according to the Soxhlet extraction protocol for solid sorbent modules.

7.2 Internal standards addition:

7.2.1 Prepare an internal standard solution containing 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Dissolve 200 mg of each compound in a small amount of methanol or carbon disulfide. Quantitatively transfer the standards to a 50-mL volumetric flask and dilute to the mark with methylene chloride. The resulting solution will contain each internal standard at a concentration of 4,000 ng/µL.

7.2.2 Spike each 1.0 mL sample extract undergoing analysis with 10 µL of the internal standard solution. This results in an internal standard concentration of 40 ng/µL each in the sample extracts.

8.0 RECOMMENDED GC/MS OPERATING CONDITIONS

Mass range: 35-500 amu

Scan time: 1 sec per scan or less

Initial column temperature: 40 °C held for 3 min

Column temperature program: 40-300 °C at 10 °C/min

Final column temperature hold: 300 °C until benzo[g,h,i] perylene has time to elute.

Injector: Split/splitless, Grob-type

Injector temperature: 270-290 °C

Injection mode: Splitless with a 0.75 to 1 min vent delay.

Sample volume: 1-2 µL

Transfer-line temperature: 250-300 °C

Ion-source temperature: As per manufacturer's specifications.

Carrier gas: Helium at 30 cm/sec or hydrogen at 50 cm/sec.

9.0 GC/MS CALIBRATION

9.1 DFTPP tuning - Each GC/MS system should be hardware tuned to meet the tuning criteria given in Table III-E-1 for a 50 ng injection of DFTPP. Background subtraction routines should be straightforward and designed only to eliminate column bleed or instrument background noise.

9.2 Designated POHC calibration:

9.2.1 Prepare a series of calibration solutions each containing a mixture of the designated POHCs at levels of 10, 25, 40, 60, and 80 ng/µL in methylene chloride. Add the proper amount of internal standard solution (as prepared in Section 7.2.1) to each mixture to yield an internal standard concentration equal to 40 ng/µL.

9.2.2 Analyze 1 µL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each designated POHC. Calculate response factors (RFs) for each designated POHC as follows:

$$RF = (A_p C_{IS})/(A_{IS} C_p)$$

where:

A_p = Area of the characteristic ion for the designated POHC being measured.

A_{IS} = Area of the characteristic ion for a specific internal standard.

C_p = Concentration (ng/μL) of the designated POHC being measured.

C_{IS} = Concentration (ng/μL) of a specific internal standard.

9.2.3 An average response factor (RF_{avg}) should be calculated for each designated POHC. The percent relative standard deviation should also be calculated for each designated POHC using the following equation:

$$\% \text{ RSD} = 100 \left[\frac{\text{standard deviation}}{RF_{avg}}\right]$$

The % RSD for each designated POHC must be less than 25%.

9.3 Continuing calibration check - A continuing calibration check should be performed every 12 hrs. This is accomplished by analyzing the calibration solution containing 25 ng/μL of each designated POHC. The calculated response factors for the designated POHCs are compared to the average response factors of the initial calibration. The difference should be less than 25%. If values greater than 25% are obtained, corrective action must be taken. Also, the relative retention times of each designated POHC in each calibration run should agree within 0.06 relative retention time units. If the retention time for any internal standard changes by more than 30 sec from the last calibration check, the chromatographic system must be inspected for malfunctions and corrections made. If the EICP area for any internal standard changes by a factor of two (-50% to +100%) from the last daily continuing calibration check, the GC/MS system must be inspected for malfunctions and corrective action taken.

10.0 SAMPLE ANALYSIS

10.1 It is recommended that the extract be screened using the total chromatographable organics (TCO) procedure using the same type capillary column. This will help minimize contamination of the GC/MS system from samples containing high concentrations of organic compounds.

10.2 Spike the 1-mL extract obtained from sample preparation with 10 μL of the internal standard solution (see Section 7.2) just prior to analysis.

10.3 Analyze 1-2 μL of the spiked extract by GC/MS using the conditions outlined in Section 8.0.

10.4 If any response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the extract must be diluted. Additional internal standard solution must be added to the diluted extract to maintain a concentration 40 ng/μL of each internal standard. The diluted extract is then reanalyzed.

10.5 Perform all qualitative and quantitative data interpretations as specified in Section 11 of this procedure. Store the remainder of the extracts at 4 °C in capped vials equipped with unpierced Teflon-lined septa.

11.0 QUALITATIVE AND QUANTITATIVE DATA INTERPRETATION

Table III-E-2 summarizes the data interpretation options outlined in this procedure. Each option is discussed in detail below.

11.1 Option 1:

11.1.1 Qualitative analysis:

11.1.1.1 An analyte (i.e., designated POHC) is identified by comparison of the sample mass spectrum with a reference mass spectrum of a standard of the suspected designated POHC. The reference mass spectrum should be obtained on the user's GC/MS within the same 12 hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from calibration standards. The two criteria that must be satisfied to verify identification are: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC; and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

11.1.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12 hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the POHC of interest.

11.1.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.1.1.4 The relative intensities of ions specified in Paragraph 11.1.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)

11.1.2 Quantitative analysis:

11.1.2.1 When a designated POHC has been identified, the quantitation of that POHC will be based on the integrated abundance from the

Table III-E-2. Data Interpretation Options

Option	Designated POHC		Non-designated POHC	
	Qualitative	Quantitative	Qualitative	Quantitative
1	yes	yes	no	no
2	yes	yes	yes	semi-quantitative
3	yes	yes	yes	yes

EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

11.1.2.2 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})\ (V_T)}{(A_{IS})\ (RF)\ (V_i)}$$

where:

A_x = Area of the characteristic ion of the designated POHC measured.

I_{IS} = Amount of internal standard injected (ng).

V_T = Volume of total extract, taking into account dilutions (μL).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

V_i = Volume of extract injected (μL).

11.2 Option 2:

11.2.1 Qualitative analysis:

11.2.1.1 Designated POHCs: An analyte (i.e., designated POHC) is identified by comparison of the sample mass spectrum with a reference mass spectrum of a standard of the suspected designated POHC. The reference mass spectrum should be obtained on the user's GC/MS within the same 12 hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from calibration standards. The two criteria that must be satisfied to verify identification are: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC; and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

11.2.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12 hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total-ion chromatogram, the RRT should be assigned by using extracted-ion-current profiles for ions unique to the POHC of interest.

11.2.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.2.1.4 The relative intensities of ions specified in Paragraph 11.2.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%.

11.2.1.5 Non-designated POHCs: For samples containing components which are not designated POHCs, a library search may be made for the purpose of tentative identification. All non-designated POHC peaks which have peak heights greater than 10% of the peak height of the nearest internal standard should be searched. Computer-generated library routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass-spectral-interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.2.2 Quantitative analysis:

11.2.2.1 Designated POHC:

11.2.2.2 When a designated POHC has been identified, the quantitation of that POHC will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

11.2.2.3 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})\ (V_T)}{(A_{IS})\ (RF)\ (V_i)}$$

where:

A_x = Area of the characteristic ion of the designated POHC being measured.

I_{IS} = Amount of internal standard injected (ng).

V_T = Volume of total extract, taking into account dilutions (μL).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

V_i = Volume of extract injected (μL).

11.2.2.4 Non-designated POHCs

11.2.2.5 Estimation of the concentration of compounds which are not designated POHCs can be made. The following equation (which is similar to the equation in paragraph 11.2.2.3) is used:

$$\text{Estimated weight (ng)} = \frac{(A_x)\ (I_{IS})\ (V_T)}{(A_{IS})\ (RF)\ (V_i)}$$

where:

A_x = Area from the total ion-current of the compound of interest.

I_{IS} = Amount of internal standard injected (ng).

V_T = Volume of total extract, taking into account dilutions (μL).

A_{IS} = Area from the total ion-current of the internal standard.

RF = Assumed to be 1.

V_i = Volume of extract injected (μL).

11.3 Option 3:

11.3.1 Qualitative analysis:

11.3.1.1 Designated POHCs: An analyte (i.e., designated POHC) is identified by comparison of the sample mass spectrum with a reference mass spectrum of a standard of the suspected designated POHC. The reference mass

spectrum should be obtained on the user's GC/MS within the same 12 hr period as the sample analysis. Standard reference mass spectra for the designated POHCs may be obtained from calibration standards. Two criteria must be satisfied to verify identification: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard POHC, and (2) the mass spectrum of the sample component must match the mass spectrum of the designated POHC.

11.3.1.2 The sample component RRT must compare within ±0.06 RRT units of the RRT of the standard POHC. For reference, the standard must be run within the same 12 hr period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total-ion chromatogram, the RRT should be assigned by using extracted-ion-current profiles for ions unique to the POHC of interest.

11.3.1.3 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.3.1.4 The relative intensities of ions specified in Paragraph 11.3.1.3 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)

11.3.1.5 Non-designated POHCs: For samples containing components which are not designated POHCs, a library search may be made for the purpose of tentative identification. All non-designated POHC peaks which have peak heights greater than 10% of the peak height of the nearest internal standard should be searched. Computer-generated library routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample spectra with the nearest library searches will the mass-spectral-interpretation specialist assign a tentative identification. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

11.3.2 Quantitative analysis:

11.3.2.1 Designated POHC:

11.3.2.2 When a designated POHC has been identified, the quantitation of that POHC will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will be by the internal standard technique. The internal standard nearest in retention time to that of the designated POHC should be used for quantitation.

11.3.2.3 The total weight in nanograms of a designated POHC present in a sample may be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})\ (V_T)}{(A_{IS})\ (RF)\ (V_i)}$$

where:

A_x = Area of the characteristic ion of the designated POHC being measured.

I_{IS} = Amount of internal standard injected, (ng).

V_T = Volume of total extract, taking into account dilutions, (μL).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the designated POHC being measured.

V_i = Volume of extract injected, (μL).

11.3.2.4 Non-designated POHCs

11.3.2.5 For the quantitation of non-designated POHCs, prepare a series of calibration standards containing a mixture of each non-designated POHC corresponding to 10, 25, 40, 60, and 80 ng/μL in methylene chloride. Add the proper amount of internal standard solution (as prepared in Section 7.2.1) to each mixture to yield an internal standard concentration equal to 40 ng/μL. Analyze the standards using the GC/MS conditions given in Section 8.0.

11.3.2.6 Calculate response factors (RFs) for each non-designated POHC as follows:

$$RF = \frac{(A_N\ C_{IS})}{(A_{IS}\ C_N)}$$

where:

A_N = Area of the characteristic ion for the non-designated POHC being measured.

A_{IS} = Area of the characteristic ion for the internal standard.

C_{IS} = Concentration (ng/μL) of the internal standard.

C_N = Concentration (ng/μL) of the non-designated POHC being measured.

11.3.2.7 The total weight in nanograms of a non-designated POHC present in a sample can be calculated from the following equation:

$$\text{Total weight (ng)} = \frac{(A_x)\ (I_{IS})\ (V_T)}{(A_{IS})\ (RF)\ (V_i)}$$

where:

A_x = Area of the characteristic ion of the non-designated POHC being measured.

I_{IS} = Amount of internal standard injected, (ng).

V_T = Volume of total extract, taking into account dilutions, (μL).

A_{IS} = Area of the characteristic ion for the internal standard.

RF = Response factor for the non-designated POHC being measured.

V_i = Volume of extract injected, (μL).

12.0 QUALITY CONTROL

12.1 Each laboratory that uses these methods should operate a formal quality control program. The minimum requirement of this program should consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples. When results of sample spikes indicate atypical method performance, a QC check standard (25 ng/μL designated POHC calibration standard) must be analyzed to verify that the measurements were performed in an in-control mode of operation.

12.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

12.3 Each day that analysis is performed, the daily calibration standard should be evaluated to determine if the chromatographic system is operating properly. Two questions should be asked concerning the calibration standard--do the peaks look normal? is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate if the column is still good, the injector is leaking, the injector septum needs replacing, etc. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. If any changes are made to the system (i.e., column changed), the system must be recalibrated.

12.4 Required instrument QC is found in the following sections of this method:

12.4.1 The GC/MS system must be tuned to meet DFTPP tuning criteria as specified in Section 4.3 and 9.1.

12.4.2 There must be an initial calibration of the GC/MS system for the designated POHC as specified in Section 9.2.

12.4.3 A continuing calibration check must be carried out at least once every 12 hrs as specified in Section 9.2.

13.0 REFERENCES

13.1 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., Method 8270, NTIS No. PB88-239223, February 1987.

13.2 40 CFR Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, Method 625," October 26, 1984.

13.3 Provost, L.P. and Elder, R.S., "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

13.4 Eichelberger, J.W.; Harris, L.E.; and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

13.5 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act. Appendix A--Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater." Federal Register, Vol. 49, No. 209, Washington, D.C., October 26, 1984, pp. 141-174.

13.6 Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

GRAVIMETRIC ANALYSIS OF ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Scope: This gravimetric procedure outlines the quantitative determination of organic compounds which have boiling points of 300 °C or greater. The method involves evaporating liquid samples at room temperature to a constant weight.

1.2 Application: This procedure may be used with organic extracts of MM5 or SASS samples. Any organic solvent used to extract samples should have high volatility and a good extraction efficiency for high-boiling organic compounds. A recommended solvent is methylene chloride.

1.3 Sensitivity and detection limits: The sensitivity of the method is primarily limited by the accuracy of the balance and practical limitations on the size of the sample. A sample size larger than five milliliters should be avoided because loss of sample may occur as solvent rises up the sides of the container during the evaporation process.

2.0 SUMMARY OF METHOD

Aluminum sample dishes are cleaned, dried, and weighed to an accuracy of ±0.1 mg constant weight. One-milliliter aliquots of the sample extract, which have been adjusted to a known final volume (usually 10 mL), are placed in aluminum sample dishes. The samples are allowed to evaporate to dryness. The dishes containing the sample residues are then weighed at select intervals until constant weights are obtained. The residue weights are then calculated.

3.0 REAGENT AND MATERIALS

3.1 Methylene chloride: "Distilled in glass" or spectroscopic grade

3.2 Methanol: "Distilled in glass" or spectroscopic grade

3.3 Water: Deionized

3.4 Silica gel: Indicating type

3.5 Desiccator: Or desiccating cabinet (depending upon sample volume). Silicone grease should not be used as a sealant for desiccator due to the possibility of contamination of sample.

3.6 Drying oven: Operation to 175 °C

3.7 Aluminum weighing dishes: Approximately 57-mm diameter and 1.5 grams

3.8 Volumetric pipets: Class A (1,3,5 mL)

3.9 Forceps: Straight-blunt-specimen type

4.0 ANALYTICAL PROCEDURE

A reagent blank and duplicate aliquots from the extract should be analyzed by the following procedure.

4.1 Label aluminum sample dishes on the bottom using a ballpoint pen or a sharp object. Rinse the sample dishes first with distilled water, then methanol, and finally with methylene chloride. Handle the dishes only with tweezers.

4.2 Dry the sample dishes in a clean oven at 105-120 °C for approximately 1 hr. Remove the dishes from the oven and allow them to cool to ambient temperature in a desiccator over silica gel.

4.3 Weigh the dishes to an accuracy of ±0.1 mg.

4.4 Transfer a 1.0-mL aliquot of the sample extract into a sample dish. Evaporate the sample to visual dryness at room temperature in a hood. Make sure that no foreign particles enter the dish.

4.5 Place the sample dish in a desiccator over silica gel and allow to dry for approximately 8 hrs.

4.6 Weigh sample residue and dishes at approximately 2-hr intervals until successive values differ by less than ±0.1 mg.

5.0 CALCULATIONS

5.1 Gravimetric range organics (GRAV) - calculated using the following equation:

$$GRAV_{measured} = \frac{(\text{sample + dish weight}) - (\text{dish weight}) \times \text{total sample volume}}{\text{Aliquot volume}}$$

5.2 Corrected GRAV weights - calculated using the following equation:

$$GRAV_{corrected} = GRAV_{measured} - GRAV_{blank}$$

6.0 QUALITY ASSURANCE/QUALITY CONTROL

6.1 Precision: Duplicate analyses should be performed on each blank and sample. Each value of a duplicate analysis should agree to within ±20% of the average. If not, the analysis should be repeated.

6.2 Analytical blanks: A reagent blank consisting of the same lot of solvent used to extract samples should be analyzed along with each set of samples. Each new lot of solvent should be analyzed prior to use for extraction of samples. The volume of the solvent blank should be the same as that used for the samples. The blank should be prepared in a manner identical to the samples (i.e. concentrated).

6.3 Moisture contamination: To prevent error in weight due to moisture condensation, dishes must appear visually dry and be weighed immediately upon removal from the desiccator.

7.0 REFERENCES

7.1 Harris, J.C. et al., "Laboratory Evaluation of Level 1 Organic Analysis Procedures," EPA-600/7-82-048, NTIS No. PB82-239 294, 30-36 pp, June 1982.

7.1 Lentzen, D.E. et al., "IERL-RTP Procedures Manual: Level 1 Environmental Assessment," 2nd ed., EPA-600/7-78-201, NTIS No. PB293-795, October 1978.

HPLC/UV SCREENING METHOD FOR NON-VOLATILE ORGANIC COMPOUNDS

1.0 SCOPE AND APPLICATION

1.1 Scope: This procedure outlines a generalized approach to the screening of extracts for non-volatile designated POHCs and other non-volatile organic compounds. The method is based on separation of the components of interest by high-performance liquid chromatography with ultraviolet detection. This method is applicable to the analysis of solvent extractable organics from MM5 or SASS train sorbent modules. Extract cleanup or fractionation may be necessary to eliminate semivolatile organic compounds prior to screening for non-volatile organic compounds. This method is designed for the analysis of non-volatile compounds which are not easily amenable to GC analysis. In general, any compound which can be eluted from the analytical column under a given set of conditions and has a reasonable UV-absorbance at the analytical wavelength can be detected by this method.

1.2 Sensitivity: The sensitivity of the analytical method for a particular non-volatile organic compound depends on the level of interferences and the presence of detectable levels of that specific compound in blanks. The range of sensitivity of this procedure, defined as the slope of a plot of area response versus concentration, is dependent on the HPLC column and detector used. The range of sensitivity should be verified regularly.

The upper limit of the range is dependent on column capacity and detector nonlinearity. The upper limit can be extended by dilution of sample extracts with methylene chloride.

The lower limit of the range is determined by the minimum detectable concentration of standards. The minimum detectable limit is defined as 5x the signal-to-noise ratio.

1.3 Precision: Duplicate results by the same analyst should not differ by more than 15%.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the Soxhlet Extraction Method. A 10-50 µL aliquot of the sample extract is analyzed using high performance liquid chromatography with ultraviolet detection at 254 nm. The method is applicable to the analysis of non-volatile organic extractables from an MM5 or SASS train. The analytical method uses a C_{18} reversed-phase column and an acetonitrile/water solvent gradient.

3. INTERFERENCES

3.1 Any compound which can be eluted from the analytical column under the given chromatographic conditions and which has a significant UV absorbance at the wavelength of analysis may interfere with the analysis of a specific designated POHC.

3.2 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of a blank to check for cross-contamination.

3.3 The analytical system must be demonstrated to be free from contamination under the conditions of the analysis. This is accomplished by analyzing a laboratory reagent blank.

4.0 APPARATUS AND MATERIALS

4.1 High performance liquid chromatograph: An analytical system complete with a binary-solvent-delivery-system, gradient-programming capabilities, and all required accessories including syringes, gases, analytical columns, and solvents.

4.2 UV VIS detector - Variable or fixed wavelength (set at 254 nm).

4.3 Column - μBondapak C_{18}, 300-mm x 3.9-mm-ID or equivalent.

4.4 Integrator - Must be interfaced to UV/VIS detector to obtain peak-area measurements.

5.0 REAGENTS

5.1 Mobile phase solvents:

5.1.1 Acetonitrile - HPLC grade or better.

5.1.2 Water - Reagent grade, ASTM Type 1 or better.

5.2 Methylene chloride - "Distilled-in-Glass" or "Nanograde" or equivalent purity.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected using the appropriate sampling method as specified in the approved site test plan for the incinerator trial burn. Generally, the sampling methods are from or are similar to sampling methods specified in SW 846, Test Methods for Evaluating Solid Waste.

7.0 SAMPLE PREPARATION

7.1 Samples should be prepared according to the Soxhlet Extraction Method for Solid Sorbent Modules.

8.0 RECOMMENDED HPLC/UV OPERATING CONDITIONS

8.1 Screening conditions:

Column: μBondapak C_{18}, 300-mm x 3.9-mm-ID or equivalent.

Solvent A: Water

Solvent B: Acetonitrile

Solvent program: 15% B/85% A for 5 min, then programmed from 15% B to 100% B at 4% B per min, and hold at 100% until all components of interest elute.

Flow rate: 1 mL/min

Detector: Ultraviolet detection at 254 nm.

Injection volume: 10 to 50 μL

8.2 Operating conditions for designated POHCs: The conditions given in Section 8.1 are a generalized set of conditions for screening purposes. These conditions may require modification to allow for the separation and quantitation of a specific designated POHC.

9.0 CALIBRATION

9.1 Standards preparation: Standards are prepared to cover the linear working range of the analytical system. A minimum of five standards are prepared to cover the linear working range.

9.1.1 Stock standard: A stock standard is prepared by weighing approximately 100 mg of each designated POHC into a 10-mL volumetric flask and diluting to a total volume of 10 mL with methylene chloride.

9.1.2 Calibration standards: Calibration standards are prepared by making serial dilutions of the stock standard. A minimum of five calibration standards should be prepared.

9.2 Standards analysis: Standards are analyzed in duplicate using the conditions outlined in Section 8.0. Peak areas versus concentration are plotted.

10.0 SAMPLE ANALYSIS

10.1 A 10-50-µL aliquot of the sample extract is injected into the HPLC using the conditions given in Section 8.0.

10.1.1 Designated POHCs determination: Peak areas for designated POHCs are measured and a corresponding concentration is calculated. If the calculated value is outside the linear working range, the sample extract must be concentrated or diluted as needed, and reanalyzed.

10.1.2 Non-designated POHCs: Peak areas for non-designated peaks are measured and a corresponding concentration is estimated. The UV-response of a non-designated POHC is assumed to be equal to the UV-response of the nearest eluting designated POHC.

10.2 Solvent blank: A solvent blank treated in the same manner as a sample extract, must also be analyzed. Sample concentrations must be corrected for solvent blank contributions.

11.0 CALCULATIONS

11.1 Calibration curves are constructed by fitting a linear regression equation to the results of the analysis of calibration standard solutions. The following equation is used:

$$A_i = M\,(C_i) + B \qquad (11.1\text{-}1)$$

where:

A_i = UV area response for compound i.

C_i = Concentration of compound i.

M = Slope of the line.

B = Intercept of the line.

A correlation coefficient of greater than 0.97 must be obtained.

11.2 The concentration of compounds in the blank and sample extracts are determined by inserting the UV area response into equation 11.1-1 and calculating the concentration.

11.3 Corrected sample extract concentrations are determined using the following equation:

$$C_{corrected} = C_{measured} - C_{blank}$$

Results of an analysis should be reported in the appropriate units.

12.0 QUALITY CONTROL

12.1 Each laboratory that uses these methods should operate a formal quality control program. The minimum requirement of this program should consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples. When results of sample spikes indicate atypical method performance, a QC check standard (a mid-range designated POHC calibration standard) must be analyzed to verify that the measurements were performed in an in-control mode of operation.

12.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

12.3 Duplicate results by the same analyst should not vary by more than 15%.

12.4 Correlation coefficients for the calibration curves should be greater than 0.97.

13.0 REFERENCES

13.1 Test Methods for Evaluating Solid Waste, SW 846, 3rd ed., NTIS No. PB88-239223, Method 8310, February 1987.

13.2 James, R. et al., POHC Analysis Methods for Hazardous Waste Incineration, Volume 1, Part 1, EPA-600/8-87-037a, NTIS No. PB87-227286, August 1987.

13.3 James, R. et al., POHC Analysis Methods for Hazardous Waste Incineration, Volume 1, Part 2, EPA-600/8-87-037b, NTIS No. PB87-227294, August 1987.

13.4 James, R. et al., POHC Analysis Methods for Hazardous Waste Incineration, Volume 2, EPA-600/8-87-037c, NTIS No. PB87-227302, August 1987.

IV. EXPERIMENTAL RESULTS

Preliminary evaluations of the screening protocol were carried out using three sample extracts from incinerator tests at Pine Bluff, Arkansas. These samples were methylene chloride extracts of MM5 sorbent modules. The samples were selected, not for qualitative composition, but based upon the relative quantity of emissions in each sample. The samples were screened using the proposed tiered approach for the analyses of semivolatiles and nonvolatiles. Total chromatographable organics (TCO) and total nonvolatile residue were determined in Tier 1. Figure IV-1 shows the GC/FID chromatograms obtained for the samples using the TCO protocol with area summation stopped at the C_{17}-alkane. It can clearly be seen that many semivolatile organic compounds elute after the C_{17}-alkane.

The total area of semivolatile organic compounds is summed as total semivolatile organics (TSO). This TSO value has some significance in evaluating the quantity of semivolatile compounds in a sample, however, some compounds may be common to both TSO and GRAV. Table IV-1 summarizes the TCO, TSO, and the gravimetric (GRAV) values for each sample extract. Samples 1 and 2 contained relatively low quantities of TCO. Sample three contained a high level of TCO. The quantity of residue found in the gravimetric fractions increased from 10 mg in Sample 1 to 1100 mg in Sample 3.

Reconstructed total ion chromatograms (TIC) for the GC/MS screen for semivolatiles (Tier 3B) are presented in Figure IV-2. Trace A in Figure IV-2 is a TIC of a base-neutral-acid calibration standard containing candidate compounds, surrogates and internal standards. Plot B is the total-ion chromatogram (TIC) obtained from Sample 1. The large peak at 29.2 min was determined to be di-n-octyl phthalate. Trace amounts of benzaldehyde, alkanes, and several other phthalates were also detected. Plot C is the TIC obtained from Sample 2. The peaks at 7.0, 7.7, 9.1, and 27.7 min were tentatively identified as alkanes. The peak at 29.2 min was determined to be di-n-octyl phthalate. Plot D is the TIC obtained from Sample 3. Many of the peaks in Sample 3 overloaded the capillary column. Therefore, the sample was diluted 1:10 with methylene chloride and reanalyzed. The resultant TIC is shown in Figure IV-3. Table IV-2 summarizes the tentative identifications for the labeled peaks in Figure IV-3. Many of the compounds detected are on the Appendix 8 list.

Figure IV-4 presents the chromatograms obtained using the HPLC/UV screening protocol for nonvolatile organic compounds (Tier 3C). Trace A is a chromatogram for a PAH standard. Traces B, C, and D are for Samples 1, 2, and 3, respectively. Sample 3 contained significantly higher levels of nonvolatile components than Samples 1 and 2. Identification of unknowns in the HPLC/UV chromatograms would require analyses by HPLC/MS (Tier 4C). The Tier 4C analysis was not completed during this task.

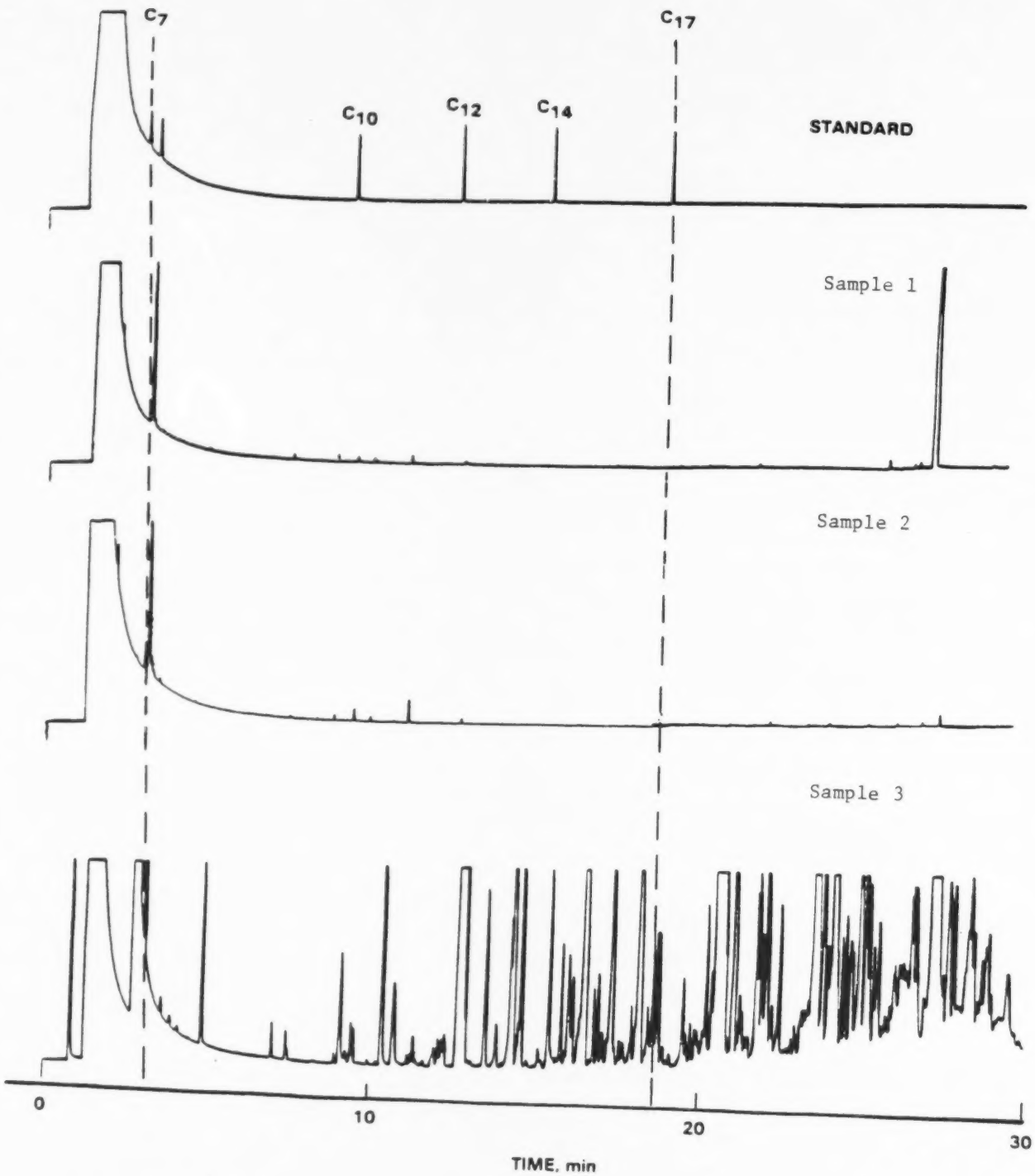

Figure IV-1. TCO screen of sample extracts from Pine Bluff, Arkansas.

Table IV-1. TCO and Gravimetric Screening Results for Pine Bluff, Arkansas, Incinerator Samples

Sample	SW 846 TCO method (mg)	Total semivolatile organics (mg)	Gravimetric (mg)
1	0.34	9.7 (0.66)*	10
2	0.39	0.67	30
3	140	360	1,100

*Total semivolatiles less total milligrams of Di-n-octyl phthalate.

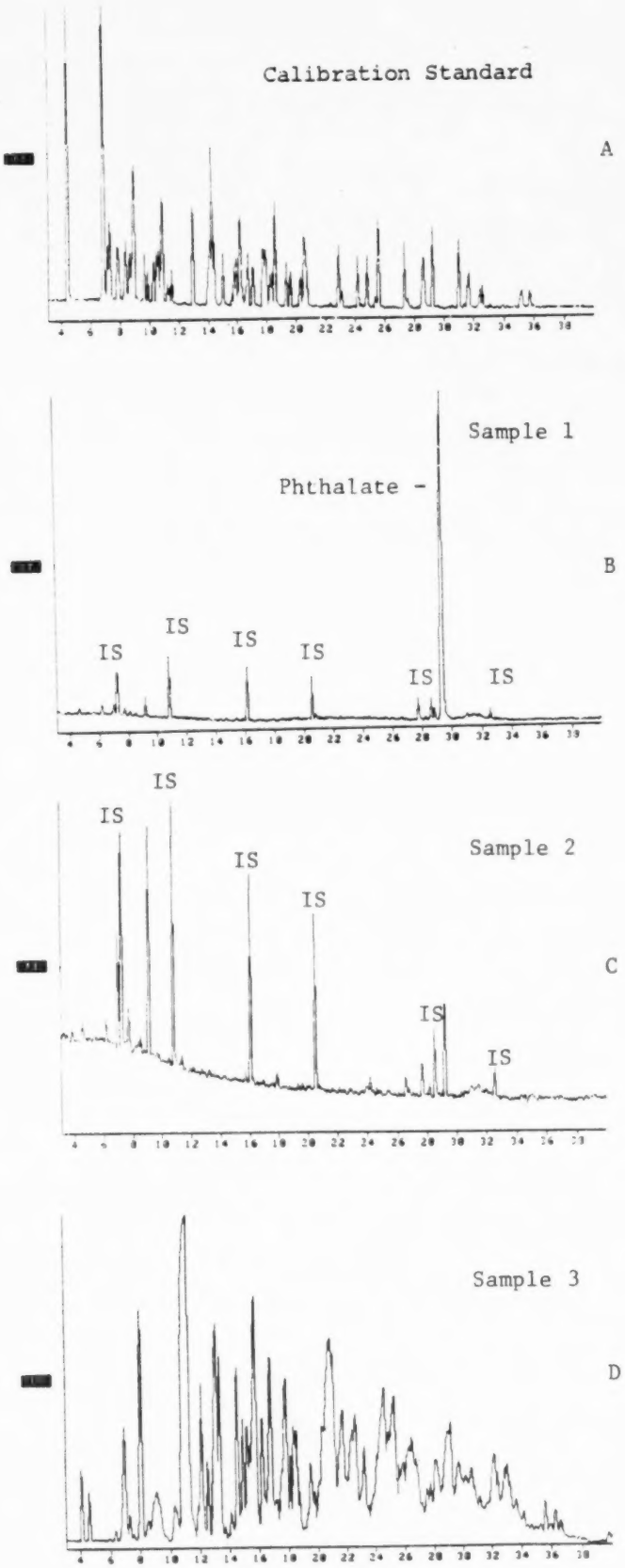

Figure IV-2. Semivolatile GC/MS screen of samples from Pine Bluff, Arkansas.

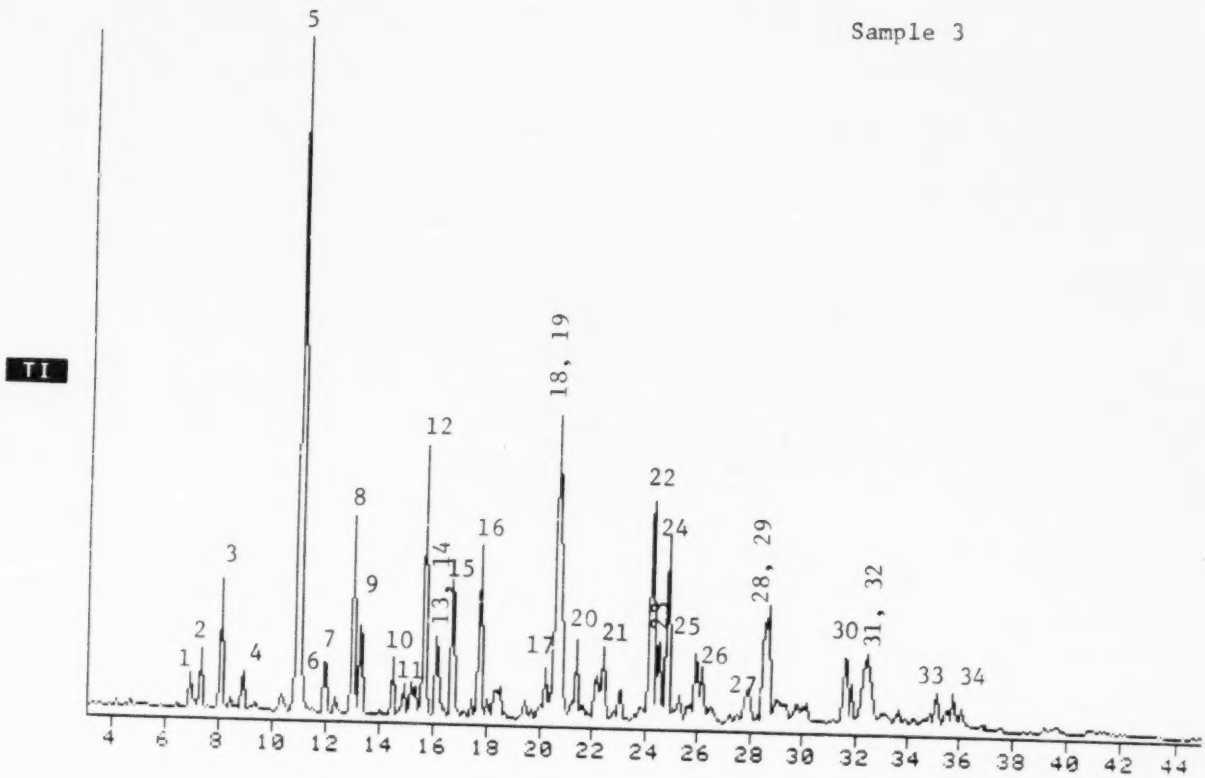

Figure IV-3. Total-ion chromatogram for 1:10 dilution of Sample 3.

Table IV-2. Tentative Compound Identifications for Peaks in Figure IV-3

Peak Number	Retention time (min)	Tentative identification
1	6.9	Phenol
2	7.3	1,4-Dichlorobenzene D-4 (IS)
3	8.0	Substituted Benzene
4	8.9	Methyl phenol
5	10.9	Naphthalene
6	10.9	Naphthalene D-8 (IS)
7	11.9	C_9H_7N
8	13.0	Methyl Naphthalene
9	13.3	Methyl Naphthalene
10	14.5	Biphenyl
11	14.9	Dimethyl Naphthalene
12	15.6	Biphenylene/Acenaphthalyene
13	16.2	Acenaphthene
14	16.2	Acenaphthene D-10 (IS)
15	16.7	Dibenzo furan
16	17.7	Fluorene
17	20.2	Dibenzothiophene
18	20.7	Phenanthrene/Anthracene
19	20.7	Phenanthrene D-10 (IS)
20	21.4	Carbazole
21	22.2	Methyl phenanthrene/Methyl/Anthracene
22	24.2	Pyrene
23	24.5	Fluoranthene
24	24.8	$C_{16}H_{10}$
25	25.9	Benzo[b] fluorene
26	26.2	Benzo[a] fluorene
27	28.5	$C_{18}H_{12}$ (Tricylic)
28	28.7	Chrysene
29	28.7	Chrysene D-12 (IS)
30	31.6	$C_{20}H_{12}$
31	32.3	Perylene
32	32.3	Perylene D-12 (IS)
33	35.1	Benzo[g,h,i]perylene
34	35.1	Ideno(1,2,3-cd)pyrene

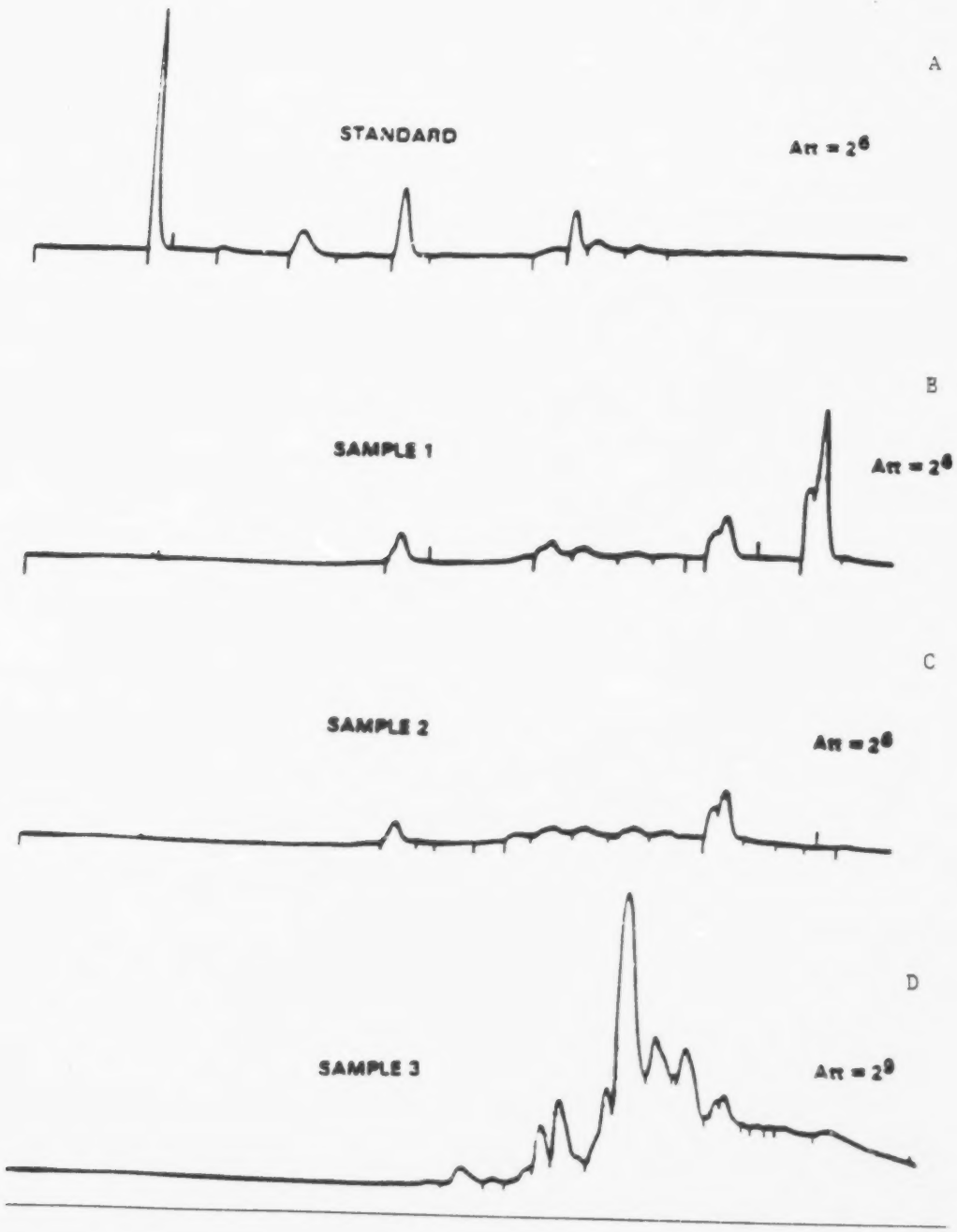

Figure IV-4. HPLC/UV screen chromatograms for the 3 samples from Pine Bluff, Arkansas.

V. QUALITY ASSURANCE SUMMARY

The work that was completed at SRI and presented in this report was performed under SRI Quality Assurance Project Plan entitled "POHC and PIC Screening" for EPA Contract 68-02-3996, Work Assignment 2/017, July 10, 1987. However, the expected number of analyses of actual environmental samples did not materialize. Only three samples from a sample repository were analyzed near the end of the work assignment period. Thus, data that were collected will not have an impact on regulatory, enforcement, legal, or policy matters. Because there were no critical measurements made on environmental samples, the QA/QC requirements commensurate with developmental work assignment are not applicable to all phases of this project. However, the QA/QC requirements for a method development or feasibility study were met.

The major effort of SRI was to develop a generalized screening protocol for the analysis of organic compounds in combustion effluents. The work assignment was directed to the review of analytical methods in the literature and to the writing of the proposed analytical protocols. In this report, SRI presents the results of a tiered approach to the screening of combustion effluents that must be the initial phase in the development of a risk-driven protocol. This task was accomplished. The draft of seven protocols with their corresponding QC requirements are presented.

Three samples extracts that were stored at EPA Pine Bluff experimental incinerator were screened using the proposed tiered approach for the analysis of semivolatiles and nonvolatiles. Specifically, total chromatographable organics, GC/MS screening for semivolatile organic compounds, gravimeteric analyses of organic compounds, and HPLC/UV screening for nonvolatile organic compounds were performed. The analyses of the three extracts were conducted under the QA/QC general guidelines for developmental research project. The QC associated with these methods included the analysis of replicate samples, methods blanks, spiked samples, surrogate spiked samples, and calibration standards. Also, the GC/MS was tuned with DFTPP and continuous calibration curves were prepared.

APPENDIX A

PREDICTED ANALYTICAL METHODS FOR POHCs

Table A-1. Predicted Analytical Methods for POHCs

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Acenaphthene, 5-nitro-	X	X		
Acetaldehyde	X	X	X	
Acetamide, N-(4-(5-nitro-2-furyl)-2-thiazolyl)-*				
2- Acetamidofluorene	X	X	X	
Acetic acid, (4-(bis(2-chloroethyl)amino)phenyl)-, cholesteryl ester*				
Acetonitrile	X	X		
Acetophenetidine			X	
Acetophenone	X	X		
3-(alpha-Acetonylbenyl)-4-hydroxycoumarin			X	
3-(alpha-Acetonylbenzyl)-4-hydroxycoumarin and salts (Warfarin)			X	
2-Acetylaminofluorene	X	X	X	
Acetyl chloride	X	X		
1-Acetyl-2-thiourea			X	
Acrolein	X	X	X	
Acrylamide	X	X		
Acrylonitrile	X	X		
Actinomycin D			X	X
Aflatoxin B-1			X	X
Aflatoxin B-2			X	X
Aflatoxin G-1			X	X

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Aflatoxin G-2			X	X
Aldrin		X		
Allyl alcohol	X	X		
4-Aminobiphenyl	X	X		
1-Amino-4-bromonaphthalene	X	X		
1-Amino-4-chloronaphthalene	X	X		
3-Amino-9-ethyl carbazole	X	X		
6-Amino-1,1a,2,8,8a,8b-hexahydro-8-(hydroxy-methyl)-8a-methoxy-5-methylcarbamate azirino[2',3':3,4]pyrrolo[1,2-a]indole-4,7-dione(ester)			X	
5-(Aminomethyl)-3-isoxazolol		X		
Amitrole	X	X		
Ammonium, (4-(p-(dimethylamino)-alpha-phenylbenzyl-idene)-2,5-cyclohexadien-1-ylidene)-dimethyl-, chloride*				
Aniline	X	X		
Aniline, 4,4'-methylenebis(N,N-dimethyl)-	X	X		
Aniline, 4,4'-methylenebis(2-methyl)-	X	X		
Aniline, 4,4'-thiodi-	X	X		
Aniline, p-(phenylazo)-	X	X		
Aniline, 2,4,5-trimethyl-	X	X		
o-Anisidine	X	X	X	
o-Anisidine hydrochloride	X	X	X	

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
o-Anisidine, 5-methyl-	X	X		
o-Anisidine, 5-nitro-	X	X		
Anthraquinone, 1-amino-2-methyl-	X	X	X	
Anthraquinone, 2-amino-	X	X	X	X
Anthraquinone, 2-methyl-1-nitro-	X	X	X	
Aramite	X	X		
Auramine O				X
Azaserine			X	
Barbituric acid, 5-ethyl-5-phenyl-			X	
Benz(c)acridine			X	
Benzaldehyde			X	
Benz(a)anthracene	X	X	X	X
Benzenamine, hydrochloride	X	X	X	
Benzene	X	X		
Benzenearsonic acid	X	X	X	
Benzene, dichloromethyl-	X	X		
Benzene, 1,2-(methylenedioxy)-4-(2-(octylsulfinyl) propyl)-	X	X		
Benzenethiol	X	X	X	
Benzidine	X	X	X	
Benzidine sulfate			X	

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Benzimidazolecarbamic acid, 1-(butylcarbamoyl)-, methyl ester	X	X	X	
Benzo(b)fluoranthene	X	X	X	X
Benzo(j)fluoranthene	X	X		
Benzo(a)pyrene	X	X	X	X
Benzonitrile, 3,5-dibromo-4-hydroxy-	X	X		
(1)Benzopyrano(3,4-b)furo(2,3-h)(1) benzopyran-6(6aH)-one, 1,2,12,12a-tetrahydro-2-alpha-isopropenyl-8,9-dimethoxy-			X	
p-Benzoquinone		X	X	
Benzotrichloride		X		
Benzyl chloride	X	X		
Biphenyl, 4-nitro	X	X		
4,4'-Bipyridinium,1,1'-dimethyl-, dichloride			X	
Bis(2-chloroethoxy)methane	X	X		
Bis(2-chloroethyl) ether	X	X		
N,N-Bis(2-chloroethyl)-2-naphthylamine	X	X		
Bis(2-chloroisopropyl) ether	X	X		
Bis(chloromethyl) ether	X	X		
Bis(2-ethylhexyl) phthalate	X	X	X	
5-Bromoacenaphthene	X	X		
Bromoacetone	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
9-Bromoanthracene	X	X		
2-Bromofluorene	X	X		
9-Bromofluorene	X	X		
Bromomethane	X	X		
1-Bromo-2-methylnaphthalene	X	X		
1-Bromo-4-methylnaphthalene	X	X		
2-(Bromomethyl)naphthalene	X	X		
2-Bromonaphthalene	X	X		
9-Bromophenanthrene	X	X		
4-Bromophenyl phenyl ether	X	X		
3-Bromoquinoline	X	X		
Brucine			X	
1,3-Butadiene, 2-chloro-	X	X		
1-Butanol, 4-(butylnitrosoamino)-	X	X		
2-Butanone peroxide		X	X	
Butyl benzyl phthalate	X	X	X	
2-sec-Butyl-4,6-dinitrophenol (DNBP)	X	X		
Carbamic acid, diethyldithio-, 2-chloroallyl ester	X	X		
Carbamic acid, methyl-,2,3-dihydro-2,2-dimethyl-7-benzofuranyl ester	X	X		
Carbamic acid, methyl-,4-dimethylamino-3,5-xylyl ester	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Carbamic acid, methyl-,2,3-(dimethyl-methylenedioxy)phenyl ester	X	X		
Carbamic acid, methyl-,1-naphthyl ester	X	X		
Carbanilic acid, m-chloro-,4-chloro-2-butynyl ester	X	X		
Carbon disulfide		X		
Carbon oxyfluoride			X	
Chloral		X	X	
Chlorambucil			X	
Chlordane (alpha and gamma isomers)		X		
Chlorinated benzenes, N.O.S.	X	X		
Chlorinated ethane, N.O.S.	X	X		
Chlorinated fluorocarbons, N.O.S.		X		
Chlorinated naphthalene, N.O.S.	X	X		
Chlorinated phenol, N.O.S.	X	X		
Chloroacetaldehyde	X	X	X	
Chloroalkyl ethers, N.O.S.	X	X		
p-Chloroaniline	X	X		
Chlorobenzene	X	X		
1-Chloroanthracene	X	X		
2-Chloroanthracene	X	X		
9-Chloroanthracene	X	X		
Chlorobenzilate	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
4-Chloro-m-cresol	X	X	X	
1-Chlorodibenzo-p-dioxin	X	X		
2-Chlorodibenzo-p-dioxin	X	X		
1-Chloro-2,3-epoxypropane	X	X		
2-Chloroethyl vinyl ether	X	X		
Chloroform	X	X		
Chloromethane	X	X		
9-(Chloromethyl)anthracene	X	X		
Chloromethyl methyl ether	X	X		
2-Chloronaphthalene	X	X		
1-Chloro-8-nitronaphthalene	X	X		
2-Chlorophenol	X	X	X	
1-(o-Chlorophenyl)thiourea			X	
3-Chloropropionitrile	X	X		
Chrysene	X	X	X	
Citrus red No. 2			X	
Coal Tars			X	
Coumarin, 3-chloro-7-hydroxy-4-methyl-, O-ester with O,O-diethyl phosphorothioate	X	X		
Creosote	X	X		
m-Cresol	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
o-Cresol	X	X		
p-Cresol	X	X		
Crotonaldehyde			X	
Crotonic acid, 2-(1-methylheptyl)-4,6-dinitrophenyl ester	X	X		
Crotonic acid, 3-hydroxy-, alpha-methylbenzyl ester, dimethyl phosphate, (E)-	X	X		
Crotonic acid, 3-hydroxy-, methyl ester, dimethyl phosphate, (E)-	X	X		
Cycasin			X	
4-Cyclohexene-1,2-dicarboximide, N-((1,1,2,2-tetrachloroethyl) thio)-	X	X		
4-Cyclohexene-1,2-dicarboximide, N-(trichloromethyl)thio-	X	X		
2-Cyclohexyl-4,6-dinitrophenol	X	X		
Cyclophosphamide			X	
Daunomycin			X	
DDD		X		
DDE		X		
Decafluorobiphenyl		X		
Decafluorotriphenylphosphine		X		
DDT		X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Diallate	X	X		
2,4-Diaminotoluene	X	X		
2,6-Diaminotoluene	X	X		
3,4-Diaminotoluene	X	X		
Dibenz(a,h)acridine	X	X		
Dibenz(a,j)acridine	X	X	X	X
Dibenz(a,h)anthracene	X	X	X	X
7H-Dibenzo(c,g)carbazole	X	X	X	
Dibenzo(a,e)pyrene	X	X	X	
Dibenzo(a,h)pyrene	X	X	X	
Dibenzo(a,i)pyrene	X	X	X	
9,10-Dibromoanthracene	X	X		
3,6-Dibromocarbazole	X	X		
1,2-Dibromo-3-chloropropane	X	X		
1,2-Dibromoethane	X	X		
Dibromomethane	X	X		
Di-n-butyl phthalate	X	X	X	
9,10-Dichloroanthracene	X	X		
m-Dichlorobenzene	X	X		
o-Dichlorobenzene	X	X		
p-Dichlorobenzene	X	X		
Dichlorobenzene, N.O.S.	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
3,3'-Dichlorobenzidine	X	X	X	
1,4-Dichloro-2-butene	X	X		
2,3-Dichlorodibenzo-p-dioxin	X	X		
2,7-Dichlorodibenzo-p-dioxin	X	X		
3,6-Dichlorodibenzofuran	X	X		
Dichlorodifluoromethane		X		
1,1-Dichloroethane	X	X		
1,2-Dichloroethane	X	X		
trans-1,2-Dichloroethene	X	X		
Dichloroethylene, N.O.S.	X	X		
1,1-Dichloroethylene	X	X		
Dichloromethane	X	X		
6,9-Dichloro-2-methoxyacridine	X	X		
2,4-Dichlorophenol	X	X	X	
2,6-Dichlorophenol	X	X	X	
2,4-Dichlorophenoxyacetic acid (2,4-D)			X	
Dichlorophenylarsine			X	
Dichloropropane, N.O.S.	X	X		
1,2-Dichloropropane	X	X		
Dichloropropanol, N.O.S.	X	X		
1,3-Dichloro-2-propanol	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Dichloropropene, N.O.S.	X	X		
1,3-Dichloropropene	X	X		
Dieldrin		X		
1,2:3,4-Diepoxybutane		X		
Diethylarsine*				
N,N-Diethylhydrazine	X	X	X	
O,O-Diethyl S-methyl ester of phosphorodithioic acid	X	X		
O,O-Diethylphosphoric acid, O-p-nitrophenyl ester	X	X		
Diethyl phthalate	X	X	X	
O,O-Diethyl O-2-pyrazinyl phosphorothioate		X		
Diethylstilbestrol (D.E.S.)			X	
Dihydrosafrole			X	
3,4-Dihydroxy-alpha-(methylamino)methyl benzyl alcohol			X	
Diisobutyl phthalate	X	X		
Diisopropylfluorophosphate (DFP)		X		
Dimethoate	X	X		
3,3'-Dimethoxybenzidine			X	
p-Dimethylaminoazobenzene	X	X		
alpha,alpha-Dimethylaminoazobenzene		X		
7,12-Dimethylbenz(a)anthracene	X	X	X	X

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
9,10-Dimethyl(1,2)benzanthracene	X	X		
3,3'-Dimethylbenzidine			X	
Dimethylcarbamoyl chloride*				
1,1-Dimethylhydrazine			X	
1,2-Dimethylhydrazine			X	
3,3-Dimethyl-1-(methylthio)-2-butanone, O-((methylamino)carbonyl)oxime [Thiofanox]*				
9,10-Dimethyl-1,2-benzanthracene	X	X		
alpha,alpha-Dimethylphenethylamine	X	X		
2,4-Dimethylphenol	X	X	X	
2,6-Dimethylphenol	X	X	X	
Di-n-butyl phthalate	X	X	X	
Dimethyl phthalate	X	X	X	
Dimethyl sulfate	X			
m-Dinitrobenzene	X	X		
p-Dinitrobenzene	X	X		
Dinitrobenzene, N.O.S.	X	X		
4,6-Dinitro-o-cresol	X	X	X	
4,6-Dinitro-o-cresol (and salts)	X	X	X	
2,4-Dinitrophenol	X	X	X	
2,4-Dinitrotoluene	X	X		
2,6-Dinitrotoluene	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Di-n-octyl phthalate	X	X	X	
1,4-Dioxane	X	X		
Diphenylamine	X	X		
Diphenylamine, 4-nitroso	X	X		
1,2-Diphenylhydrazine			X	
Di-n-propylnitrosamine	X	X		
Disulfoton	X	X		
2,4-Dithiobiuret			X	
Endosulfan		X		
Endrin (and metabolites)		X		
Epinephrine			X	
Ethanol, 2-chloro-		X		
Ether, 2,4-dichlorophenyl p-nitrophenyl	X	X		
Ethyl carbamate	X	X		
Ethyl cyanide	X	X		
Ethylenebisdithiocarbamic acid (salts and esters)*				
Ethylene diamine	X			
Ethyleneimine	X	X		
Ethylene oxide	X			
Ethylenethiourea			X	
Ethyl methacrylate	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Ethyl methanesulfonate		X		
Fluoranthene	X	X	X	X
2-Fluoraniline		X		
Fluorine			X	
2-Fluoroacetamide			X	
Fluoroacetic acid, sodium salt		X	X	
1-Fluoronaphthalene	X	X		
Formaldehyde			X	
Formic acid		X	X	
Formic acid, 2-(4-(5-nitro-2-furyl)-2-thiazolyl) hydrazide*				
Glutarimide, 3-(2-(3,5-dimethyl-2-oxocyclohexyl)-2-hydroxyethyl)-*				
Glycidylaldehyde*				
Halomethane, N.O.S.	X	X		
Heptachlor		X		
Heptachlor epoxide	X	X		
Heptachlor epoxide (alpha, beta, and gamma isomers)		X		
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	X	X		
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	X	X		
Hexabromobiphenyl	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Hexachlorobenzene		X		
Hexachlorobutadiene		X		
Hexachlorocyclohexane (all isomers)	X	X		
Hexachlorocyclopentadiene		X		
Hexachloroethane		X		
1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-endo,endo-dimethanonaphthalene		X		
Hexachlorophene		X		
Hexachloropropene		X		
Hexaethyl tetraphosphate		X		
Hydantoin, 5,5-diphenyl-			X	
Hydantoin, 5,5-diphenyl-, monosodium salt			X	
Hydrazine			X	
Hydroquinone	X	X		
Hydroxydimethylarsine oxide	X	X		
N-(2-Hydroxyethyl)ethyleneimine*				
Hydroxylamine, N-nitroso-N-phenyl-, ammonium salt	X	X		
2-Imidazolidinone, 1-(5-nitro-2-thiazolyl)-*				
Indeno(1,2,3-c,d)pyrene	X	X	X	X
Iodomethane	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
1-Iodonaphthalene	X	X		
Isocyanic acid, methyl ester	X	X		
Isobutyl alcohol	X	X		
Isonicotinic acid hydrazide			X	
Isosafrole	X	X	X	
Kepone	X	X		
Ketene	X	X		
Lasiocarpine*				
Maleic anhydride	X	X		
Maleic hydrazide		X	X	
Malononitrile	X	X		
Melphalan			X	
Methacrylonitrile		X		
Methane sulfonic acid, ethyl ester	X	X		
Methanethiol	X	X		
Methapyrilene			X	
1,3,4-Metheno-1H-cyclobuta[cd]pentalene, 1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-	X	X		
Metholmyl*				
Methoxychlor	X	X		
2-Methylaziridine		X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
3-Methylcholanthrene	X	X	X	X
Methylchlorocarbonate*				
4,4'-Methylenebis(2-chloroaniline)	X	X	X	
Methyl ethyl ketone (MEK)	X	X		
Methyl hydrazine			X	
2-Methyllactonitrile			X	
Methyl methacrylate	X	X		
Methyl methanesulfonate	X	X		
2-Methyl-2-(methylthio)propionaldehyde-o-(methylcarbonyl)oxime*				
N-Methyl-N'-nitro-N-nitrosoguanidine			X	
Methyl parathion	X	X		
Methyl phenols (3-,4-, and 2-)	X	X	X	
Methylthiouracil		X		
Methyl yellow		X	X	
Mitomycin C			X	
Mustard gas	X	X		
Naphthalene	X	X	X	
1,5-Naphthalenediamine	X	X		
1,4-Naphthoquinone	X	X		
1,4-Naphthoquinone, 2,3-dichloro-	X	X		
alpha-Naphthylamine	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
1-Naphthylamine	X	X		
2-Naphthylamine	X	X		
1-Naphthyl-2-thiourea			X	
Nicotine	X	X	X	
Nicotine (and salts)			X	
p-Nitroaniline	X	X		
Nitrobenzene	X	X		
Nitrogen mustard (and hydrochloride salt)	X	X		
Nitrogen mustard N-Oxide (and hydrochloride salt)	X	X		
Nitroglycerine	X	X		
4-Nitrophenol	X	X	X	
4-Nitroquinoline-1-oxide			X	
Nitrosamine, N.O.S.	X	X		
N-Nitrosodi-n-butylamine	X	X		
N-Nitrosodiethanolamine	X	X		
N-Nitrosodiethylamine	X	X		
N-Nitrosodimethylamine	X	X		
N-Nitroso-N-ethylurea			X	
N-Nitrosomethylethylamine	X	X		
N-Nitroso-N-methylurea			X	
N-Nitroso-N-methylurethane	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
N-Nitrosomethylvinylamine	X	X		
N-Nitrosomorpholine			X	
N-Nitrosonornicotine			X	
N-Nitrosopiperidine			X	
N-Nitrosopyrrolidine	X	X		
N-Nitrososarcosine			X	
5-Nitro-o-toluidine			X	
17-alpha-19-Norpregna-1,3,5(10)-trien-20-yn-17-ol, 3-methoxy-*				
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin	X	X		
1,2,3,4,6,7,8,9-Octachlorodibenzofuran	X	X		
Octamethylpyrophosphoramide	X	X		
7-Oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid*				
2-Oxepanone	X	X		
2-Oxetanone*				
4,4'-Oxydianiline*				
Paraldehyde		X		
Parathion		X		
Pentachlorobenzene	X	X		
1,2,3,4,7-Pentachlorodibenzo-p-dioxin	X	X		
Pentachloroethane	X	X		
Pentachloronitrobenzene (PCNB)	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Pentachlorophenol	X	X	X	
Pentafluorophenol		X		
Peroxyacetic acid*				
Phenacetin			X	
Phenol	X	X	X	
Phenylenediamine (meta, ortho, and para)	X	X		
m-Phenylenediamine, 4-chloro-	X	X		
m-Phenylenediamine, 4-methoxy-, sulfate*				
o-Phenylenediamine, 4-chloro-	X	X		
Phenylmercury acetate	X	X		
N-Phenylthiourea			X	
Phosgene	X	X		
Phosphine	X	X		
Phosphonic acid, (2,2,2-trichloro-1-hydroxyethyl)-, dimethyl ester	X	X		
Phosphonothioic acid, phenyl-, O-(4-bromo-2,5-dichlorophenyl) O-methyl ester	X	X		
Phosphonothioic acid, phenyl-, O-ethyl O-(p-nitrophenyl) ester	X	X		
Phosphoramidothioic acid, acetimidoyl-, O,O-bis(p-chlorophenyl) ester	X	X		
Phosphoric acid, 2-chloro-1-(2,4-dichlorophenyl)vinyl diethyl ester	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Phosphoric acid, 2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl ester	X	X		
Phosphoric acid, 1,2-dibromo-2,2-dichloroethyl dimethyl ester	X	X		
Phosphoric acid, 2,2-dichlorovinyl dimethyl ester	X	X		
Phosphoric acid, dimethyl ester, ester with 2-chloro N,N-diethyl-3-hydroxycrotonamide	X	X		
Phosphoric acid, dimethyl ester, ester with (E)-3-hydroxy-N,N-dimethylcrotonamide	X	X		
Phosphoric acid, dimethyl ester, ester with (E)-3-hydroxy-N-methylcrotonamide	X	X		
Phosphoric acid, trimethyl ester	X	X		
Phosphoric acid, tri-o-tolyl ester	X	X		
Phosphoric triamide, hexamethyl-	X	X		
Phosphorodithioic acid, O,O-diethyl ester, S-ester with 3-(mercaptomethyl)-1,2,3-benzotriazin-4(3H)-one	X	X		
Phosphorodithioic acid, O,O-diethyl-S-(((1,1-dimethylethyl) thio)methyl) ester	X	X		
Phosphorodithioic acid, S-(((p-chlorophenyl)thio)methyl) O,O-diethyl ester	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Phosphorodithioic acid, O,O-diethyl S-(ethylthio)methyl) ester [Phorate]	X	X		
Phosphorodithioic acid, O,O-dimethyl ester, S-ester with 3-(mercaptomethyl)-1,2,3-benzotriazin-4(3H)-one	X	X		
Phosphorodithioic acid, O,O-dimethyl ester, S-ester with N-(mercaptomethyl)phthalimide	X	X		
Phosphorodithioic acid, S,S'-p-dioxane-2,3-diyl-O,O,O',O'-tetraethyl ester	X	X		
Phosphorodithioic acid, S,S'-methylene O,O, O',O'-tetraethyl ester	X	X		
Phosphorothioic acid, O,O-diethyl O-(2-(ethylthio)ethyl) ester, mixed with O,O-diethyl S-(2-(ethylthio)ethyl) ester (7:3)	X	X		
Phosphorothioic acid, O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) ester	X	X		
Phosphorothioic acid, O,O-diethyl O-(p-(methylsulfinyl) phenyl) ester	X	X		
Phosphorothioic acid, O,O-diethyl O-(3,5,6-trichloro-2-pyridyl) ester	X	X		
Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino) sulfonyl)phenyl)ester [Famphur]	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
Phosphorothioic acid, O,O-dimethyl-, O-(4-methylthio)-m-tolyl) ester	X	X		
Phosphorothioic acid, S-(2-(ethylsulfinyl)ethyl) O,O-dimethyl ester	X	X		
Phthalic acid esters, N.O.S.	X	X		
Phthalic anhydride		X		
2-Picoline		X	X	
Polybrominated biphenyls	X	X		
Polychlorinated biphenyl, N.O.S.	X	X		
Pronamide		X		
1,3-Propane sulfone	X	X		
Propene, 3-chloro-	X	X		
Propionitrile, 2-hydroxy-	X	X		
n-Propylamine	X	X		
Propyleneimine	X	X		
Propylthiouracil		X		
2-Propyn-1-ol	X	X		
Pyridine	X	X		
Pyridine, 3-chloromethyl-, hydrochloride	X	X		
Pyridine, 2,6-diamino-3-(phenylazo)-, monohydrochloride	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
(2,3,4-gh)Pyrrolizine-2,6(3H)-dione, (4,5,8,10,12,13,13a,13b-octahydro-4,5-dihydroxy-3,4,5-trimethyl-2H-(1,6) dioxacycloundecino-*				
Reserpine			X	
Resorcinol			X	
Saccharin			X	X
Saccharin (and salts)			X	X
Safrole	X	X		
Salicylanilide, 2',5-dichloro-4'-nitro-, compd. with 2-aminoethanol(1:1)			X	
2-sec-Butyl-4,6-dinitrophenol	X	X		
Selenourea			X	
Semicarbazide			X	
Streptozotocin			X	
Strychnine			X	
Strychnine (and salts)			X	
Styrene	X	X	X	
Succinic acid, mercapto-, diethyl ester, S-ester with O,O-dimethyl phosphorodithioate	X	X		
Sulfuric acid, diethyl ester	X	X		
1,2,4,5-Tetrachlorobenzene	X	X		
1,2,3,4-Tetrachlorodibenzo-p-dioxin	X	X		

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	X	X		
2,3,7,8-Tetrachlorodibenzofuran	X	X		
Tetrachloroethane, N.O.S.	X	X		
1,1,1,2-Tetrachloroethane	X	X		
1,1,2,2-Tetrachloroethane	X	X		
Tetrachloroethene	X	X		
Tetrachlo omethane	X	X		
2,3,4,6-Tetrachlorophenol	X	X		
Tetraethyldithiopyrophosphate		X		
Tetraethyl lead	X	X		
Tetraethylpyrophosphate	X	X		
Tetramethylthiuram disulfide			X	
Tetranitromethane*				
Thioacetamide			X	
Thiosemicarbazide			X	
Thiourea			X	
Thiuram			X	
Toluene	X	X		
Toluenediamine		X		
Toluene, 2,4-diamino-	X	X		
o-Toluidine	X	X	X	
o-Toluidine, 5-chloro-	X	X	X	

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
o-Toluidine hydrochloride			X	
o-Toluidine, 4-(o-tolylazo)-	X	X		
p-Toluidine, alpha,alpha,alpha-trifluoro-2,6-dinitro-N,N-dipropyl-	X	X		
p-Toluidine, N-(2-chloroethyl)-2,6-dinitro-N-propyl-alpha,alpha,alpha-trifluoro-	X	X		
Tolylene diisocyanate		X		
Toxaphene		X		
Triazene, 3,3-dimethyl-1-(p-chlorophenyl)-	X	X		
S-Triazine, 2,4-dichloro-6-(o-chloroanilino)-	X	X		
Tribromomethane	X	X		
1,2,4-Trichlorobenzene	X	X		
1,2,4-Trichlorodibenzo-p-dioxin	X	X		
1,1,1-Trichloroethane	X	X		
1,1,2-Trichloroethane	X	X		
Trichloroethene	X	X		
Trichloromethanethiol		X		
Trichloromonofluoromethane		X		
Trichlorophenol	X	X		
2,4,5-Trichlorophenol	X	X	X	

(continued)

Table A-1 (continued)

Compound Name	GC/FID	GC/MS	HPLC/ UV	HPLC/ Fluorescence
2,4,6-Trichlorophenol	X	X	X	
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)			X	
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)(Silvex)			X	
Trichloropropane, N.O.S.	X	X		
1,2,3-Trichloropropane	X	X		
0,0,0-Triethyl phosphorothioate	X	X		
sym-Trinitrobenzene	X	X		
Tris(1-azridinyl)phosphine sulfide*				
Tris(2,3,-dibromopropyl)phosphate		X		
Trypan blue			X	
Uracil mustard			X	
Uracil, 6-propyl-2-thio-			X	
Urea, 1-ethyl-3-(5-nitro-2-thiazolyl)-			X	
Vinyl chloride	X	X		